

**Department of Environment Systems
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Master's Thesis

**The analysis of Volatile Organic Compounds
generated from compressions of plastics
with different conditions**

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Abstract

With the developing economy, the growing population and the rising people's needs for various materials, the global consumption of plastic products is increasing annually. However, huge consumption leads to a large amount of waste. During the disposal of these wastes, compression is needed. When plastics are compressed, the degradation products, some non-bound residual monomers, polymerisation chemicals, additives which might have toxic properties may be emitted as Volatile Organic Compounds (VOCs).

The overall aim of this thesis, which is based on the previous studies in our lab, is to study with three kinds of conditions which are closer to the real condition in waste-processing facilities-----1) different shapes (ball, sheet) of plastics (polyethylene-PE, polypropylene-PP, polyvinyl chloride-PVC) are compressed; 2) PVC and PE or PVC and PP are compressed together; 3) PVC and Aluminum (Al) or PVC and Iron (Fe) are compressed together----- to figure out 1) how the contact area will affect the VOCs generated during the compression; 2) whether there is a synergy effect or not when PVC and PE or PVC and PP are compressed together; 3) what change VOCs will have when PVC and Al or PVC and Fe are compressed together. GC-MS (Gas chromatography-mass spectrometry) and GC-FID (Flame-ionization detection) are used to analyze the samples of VOCs which are generated during the compression to see the types of VOCs and to compare the amount of VOCs in different samples.

The results show that 1) there is a positive correlation between the increase in the contact area and the increase in the amount of VOCs generated during the compression; 2) there is no synergy effect when PVC and PE or PVC and PP are compressed together; 3) new VOCs are generated during the compression of PVC + Al or PVC + Fe.

In conclusion, there are various conditions that will affect the products of the compression of plastics. And there are a variety of products which still need to be explored. Considering the extensive dispersion and production of plastics, it is important to further study the compression of plastics.

Table of Contents

Abstract

Table of Contents

1.Introduction-----	3
1.1 plastics-----	3
1.2 plastic waste and problems-----	5
1.3 previous researches-----	7
2.Objectives-----	13
3. Mechanism-----	14
4.Experimental-----	19
4.1 Main equipment and materials-----	19
4.2 Methods-----	24
5.Results and discussion-----	28
5.1 Results of GC-MS-----	28
5.2 Calibration Curve-----	42
5.3 Results of GC-FID-----	43
5.4 Others-----	63
6. Conclusions and outlook-----	64
Acknowledgements-----	66
References-----	67

1 Introduction

1.1 Plastics

Plastics is a general term for polymer products. Polymers are large molecules or macromolecules, composed of many polymerizing monomers. In need for polymerization, initiators, catalysts, and also solvents, etc. may be used. And in order to make the plastic products get some special desired properties, a variety of additives will be put into use, for instance, plasticisers, antioxidants, light stabilisers, lubricants, pigments and fillers.

Plastics are extremely diverse in terms of composition, properties and possible applications. Thus along with the development of economy, the growth population and people's needs for various materials, the global consumption of plastic products is increasing annually since plastic materials started on an industrial scale in 1940s. The plastics production ramped up from 1.5 million tons in 1950 to 322 million tons in 2015 (**Figure 1.1-1**). And this growth trend will remain for the foreseeable future. In the whole plastics production, polyolefins account for more than 55% of global plastics materials demands such as polyethylene (PE, about 32%) which is frequently used in the production of bags, bottles, and packaging for milk, detergent and oil, etc.; Polypropylene (PP, about 24%) which is used widely for packaging, plastic containers, and bottle tops, etc.; Polyvinyl chloride (PVC, about 16%) which has many uses in such things as food wrap, vegetable oil bottles, and medical devices, etc. is the second largest resin type following polyolefins [1] (**Figure 1.1-2**).

Plastics are indispensable in our daily life which can offer many benefits for human health and the environment. For example, plastic packaging can protect food and goods from getting wasted or contaminated, thereby can save resources.

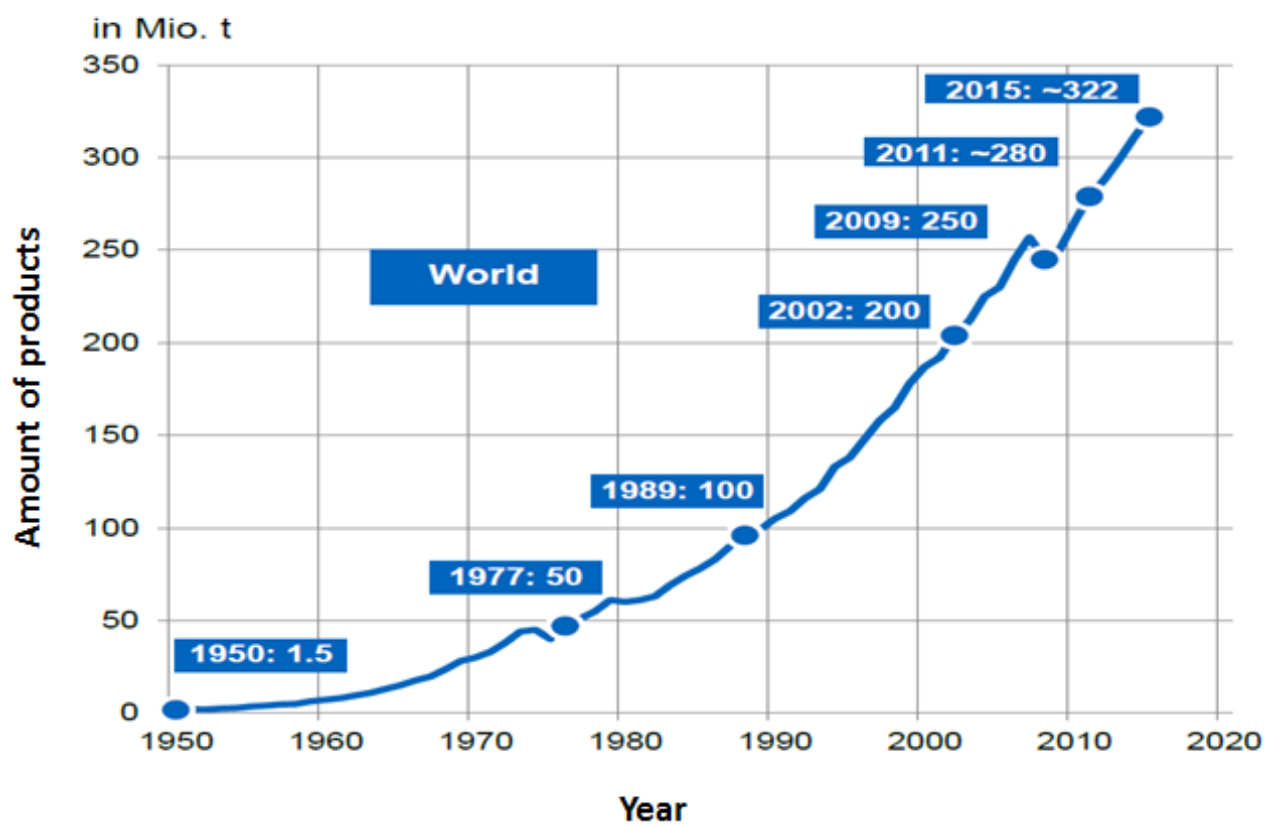


Figure 1.1-1 World plastics production 1950-2015[1]

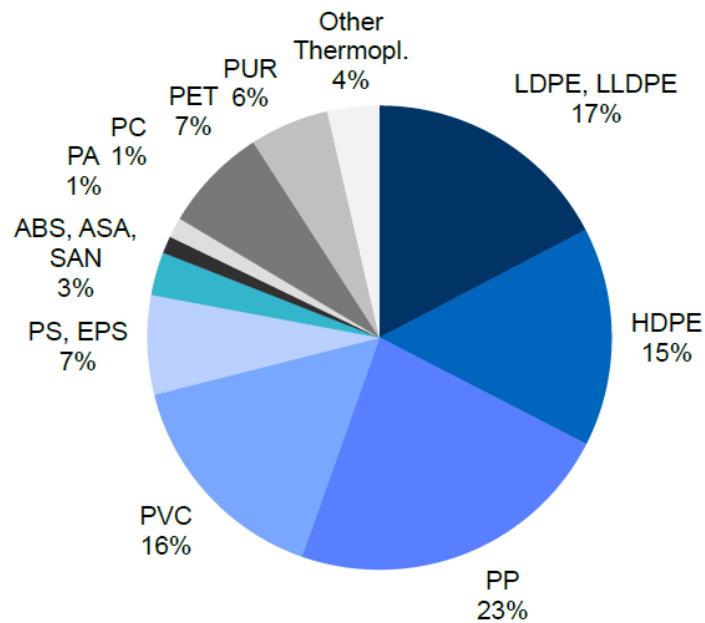


Figure1.1-2. world plastics materials demand 2015 by types[1]

(LDPE: low-density polyethylene; LLDPE: linear low-density polyethylene; HDPE: high-density polyethylene;

PP: polypropylene; PVC: polyvinyl chloride; PS: polystyrene; EPS: expanded polystyrene;

ABS: acrylonitrile butadiene styrene; ASA: acrylonitrile styrene acrylate; SAN: acrylonitrile styrene; PA: polyamide;

PC: polycarbonate; PET: polyethylene terephthalate; PUR: polyurethane.)

1.2 Plastic waste and problems

Plastics are playing an extremely important role in our modern society; however, consumption leads to waste, most of the plastic products are discarded after a short service life. Finally the large consumption of plastics resulted in a large volume of plastic waste. What is worse, only a few types of plastics are biodegradable; others are extremely persistent and usually have to take a long time to be degraded by various factors such as light, heat, oxidation, sulphur dioxide, nitrogen oxide, ozone and mechanical shear[2]. Though plastic polymers are usually not considered as toxic,

however, the degradation products of polymers and some compounds in plastic products, which can be non-bound residual monomers, polymerisation chemicals, and additives such as polyhalogenated flame retardants, might have toxic properties.^[3] Plastic waste is considered as a serious social problem.

Most of the plastic waste goes to landfill. Some parts are used for composting or incineration to get energy. And recycling is possible for some fractions. However whether finally goes to landfill or energy recovery and recycling, transportation over long distance is needed, some even exported from industrial countries to developing countries, particularly in Asia^[8]. With the increasing production of plastics, the amount of the plastics waste is also increasing. In order to reduce the volume of waste, to cut down the cost of transportation of the waste and to reduce the pollution caused by the transportation, many waste-processing facilities are built. Taking the Suginami waste-processing facility for example; it has to deal with about 180t of non-combustible waste (at most about 270t a day)^[15]. And over 50% percent of these waste is plastics.

However, when waste is compressed in waste-processing facilities, various VOCs will be generated. Many of these VOCs produced from the plastic products are hazardous for human health and the environment, such as the Suginami Disease which is caused by the operation of a waste-processing facility in Suginami Ward. In April 1996, after the facility was built to compress household waste, several hundred residents--- about 10 percent of the community living within five hundred meters of the facility---began reporting suffering a series of symptoms such as eye and skin irritation, chest pain, respiratory problems, headaches and dizziness. And a few have been hospitalized. The authorities blamed the leaks of hydrogen sulfide in the water, while

their symptoms bear a strong resemblance to those observed as multiple chemical sensitivity, thus a citizens' group blamed toxic fumes from plastics, for instance, isocyanates. [4]Some methylbenzene isocyanate, also called toluene isocyanate, was detected near the facility with GC-MS(Gas chromatography–mass spectrometry). Since this is a compound which is not usually circulating, it is presumed to be the isocyanate which arose by mechanochemical reaction. [5] which can be induced by an enormous mechanical action like the compression in the waste-processing facilities and will result in generating free radicals and subsequent chemical transformations.

However, the Environmental Dispute Coordination Commission said it was unable to specify which chemicals had contributed to Suginami Disease.

1.3 Previous Researches

In our lab, one hypothesis had been put up that when plastics are compressed in the waste-processing facilities, some volatile organic compounds (VOCs) will be produced during the degradation of polymers by the mechanism of mechanochemical reaction.

Any methods causing mechanical breakdown of polymers may produce mechanoradicals. Thus in our lab's previous researches, we suppose that when plastics are under an enormous pressure or friction, polymer molecules will react mechanochemically, then degrade, producing a series of VOCs. And this may be the reason of the Suginami Disease.

1.3.1.Hirata's study^[12]

According to Hirata's research, in the case of friction of plastics in the air, different types of plastics will emit various types of VOCs as follows. (Table1.3.1-1.)

And Hirata also made a comparison with the VOCs products of friction of plastics and the VOCs products of the thermal degradation of plastics which showed that these two kinds of VOCs are different. And also that oxygen will influence the types and amount of the VOCs generated in the experiment.

Table1.3.1-1. VOCs produced from the friction of different plastics

Materials	VOCs	average generating-amount(n=5) (ppb)
PE	Ethyl acetate	35
	Hexane	6
	Isopropyl alcohol	19
	Toluene	18
PS	Butane	135
	Hexane	114
	Isobutane	32
	Methyl ester acetic acid	26
	Toluene	60
PVC	Benzene	2
	Carbon disulfide	2
	Hexane	2
	Toluene	6
ABS	Ethylbenzene	3
	Diethyl ether	4
	Styrene	12
	Toluene	4
	4-ethenyl-cyclohexene	4
PET	---	---
PU	Acetaldehyde	8
	Ethyl acetate	8
	Toluene	27

1.3.2 Sakiyama's research^[13]

According to Sakiyama's research, VOCs produced with different conditions are compared (a. just put plastics in the air without compression; b) friction; c) compression; d) broken plastics with compression). Results are listed as follows. (Table 1.3.2-1 and Table 1.3.2-2)

Results in his research show that even when plastics are just put in the air, they will emit some VOCs. And because the VOCs produced from compression are different with those from friction, it can be deduced that the mechanism of how VOCs are produced from friction and compression might be different.

Table 1.3.2-1. VOCs produced from PE with different conditions

In the air	Friction	Compression	Broken
Octane Decane Dodecane	Isopropyl alcohol Ethyl acetate Hexane Benzene Toluene	4-pentanal 2,3,4-trimethylhexane Benzene Decane Dodecane	Hexane Cyclohexane Ethylbenzene Xylene Undecane Dodecane Hexanal

Table 1.3.2-2. VOCs produced from PVC with different conditions

In the air	Friction	Compression	Broken
Hexane Nonane Hexanal Tetrachloroethylene Chloroform 1,2-dichloroethane	Carbon disulfide Hexane Benzene Toluene	Chloroform Benzene Toluene Benzaldehyde	Cycloheptane Acetaldehyde 1,3,5-trichlorobenzene Tetrahydrofuran 1,3-butadienol

1.3.3 Nakashima's research^[14]

According to Nakashima's research, compared with the results of Hirata's research, plastics without any additives produce less VOCs, especially carbon disulfide which is detected in Hirata's research is not detected. It can be deduced that carbon disulfide might come from additives like sulfur-containing antioxidants. And additives in plastics may inhibit the reaction which will produce VOCs during the friction. And he measured the temperature during the friction, as shown in Table 1.3.3-1. It shows that during the friction of plastics, there are no thermal decomposition reactions.

Table 1.3.3-1. Comparison with thermal-decomposition temperature and measured maximum temperature during the friction of PE/PVC/PU

Materials		Thermal-decomposition temperature/ °C	Maximum temperature during the friction/°C
PE	in the air	400	93.5
	in the N ₂		141
PVC	in the air	400	126.5
	in the N ₂		153
PU	in the air	200	125
	in the N ₂		189

1.3.4 Ogawa's research^[15]

According to Ogawa's research, the amount of VOCs produced from the compression of plastics in a short time is less than that emitted from the plastics' which are put in the air for a long time. (Table 1.3.4-1)

Table1.3.4-1. Comparison of the VOCs emitted from plastics in the air and that emitted from the compression of plastics

Chemical	Compression/ μg	In the air/ μg					
		0 day	1 day	2 days	3 days	5 days	9 days
Hexane	0.07	0.05	1.64	2.47	2.16	2.56	18.4
Methyl-cyclopentane	0.02	0	0.01	0.04	0.04	0.05	0.45
Toluene	0.08	0	0	0	0	0	0.21
Cyclohexane	0.16	0	0.02	0.03	0.03	0.05	0.25
Octane	0.03	0	0	0.02	0.02	0.03	0.25
Decane	0.03	0	0	0	0	0	0.1

1.3.5 Tomita's research^[16]

According to Tomita's research, when plastics are compressed after being heated at 90°C for a while, there is less VOCs generated. Especially the amount of chemicals which have a low-boiling point has decreased a lot. These chemicals might be the non-bound residuals in the plastic, such as monomers, dimers, additives or solvents, etc.

PE stored in bags emit more VOCs at a higher temperature. For instance, at 40 °C, the amount of acetone is five times of that at 10°C. When ball plastics are cut in half, it can emit more VOCs, especially some low boiling point chemicals. He deduces that it is because of the increasing surface area.

1.3.6 Koseki's research^[17]

According to Koseki's research, he puts focus on the mechanism of the compression of plastics. Average molecular weight, molecular weight distribution and the amount of residual molecules are analyzed after compression. The result shows that 1) there is just a very small difference of the average molecular weight and molecular weight

distribution after the compression, hence the possibility of a main chain scission is low. But with different methods, the results might change; 2) the amount of styrene molecules after the compression of PS is more than that before the compression. Therefore, at least, it is impossible that residual styrene molecules will emit during the compression.

The previous studies do show that when plastics are under mechanical action, whether friction or pressure, various VOCs would be produced. And plastics will emit VOCs gradually even they are just put aside. With a higher temperature, there will be more VOCs generated. Hexane, toluene, benzene, styrene are usually found in these VOCs which are also found in the atmosphere around the Suginami Ward with a relatively higher concentration than usual. These previous studies explain the reason of the Suginami Disease or the mechanism of the compression of plastics to some extent.

However there are still many problems. For example, 1) in the real non-combustible waste, there are not only one kind of plastics in it, often different kind of plastics are compressed together, and apart from plastics, there are still other kind of things, such as metals; 2) these studies have low repeatability. 3) The mechanism of the compression of plastics is still unknown.

Considering the increasing production of plastics, further study is needed.

2. Objectives

In reality, when plastics are compressed in the waste-processing facility, different shapes and different types of plastics are always mixed together. And often some kinds of metals or metal oxides are mingled together.

At this study, 1) different shape of plastics---sheet and ball plastics are used. Therefore we can see how shapes will influence the results since the contact areas are different and there is almost no friction in the sheet plastics. 2) PVC and other kind of plastics are compressed together to see whether there is a synergy effect or not since when PVC are compressed, there may be chlorine radicals ($\text{Cl} \cdot$) generated which has a relatively high reactivity to induce a series of reactions; 3) PVC are compressed with Fe and Al respectively to see how metals will affect the VOCs produced during the compression of plastics.

Based on the previous study, analyzing the VOCs produced during the compression of plastics with different conditions is important, since plastics are omnipresent and indispensable nowadays in our social life. To know what kinds of VOCs and how much of them there are and to know in what condition these VOCs will be generated may help us to avoid some mishaps like Suginami Disease in the future and may help us know how to facilitate the proper way to deal with plastics waste.

3. Mechanism

Mechanisms considered in this study are stated as follows:

3.1 Mechanochemistry

Mechanochemistry is defined as a branch of chemistry in which chemical phenomena, such as chemical reactions and changes in crystalline structures, induced by mechanical actions like fracture and large deformations. Similar with some well-established branches of chemistry, like radiation chemistry and photochemistry, mechanical energy is also a type of energy, analogous to electrical currents and photons, which can produce some chemical changes when introduced into a system.

Researchers have found that purely mechanical actions can induce a chemical phenomenon, such as the scission of chemical bonds which can produce some free radicals. Since free radicals are unstable and reactive regardless of the method used for generation, the mechanically produced free radicals then initiate a series of reactions.^[6] For example, when mechanical energy is introduced to PE, some main chain of the molecule will break randomly, then some primary radicals (a) will be generated. Some of these primary radicals are converted into the peroxy radicals (b) at 77K in the presence of oxygen. Other remaining primary radicals are gradually turning into some more stable radicals like radicals (c). And these radicals finally react to create some new chemicals. ^[6](**Figure3.1-1**)

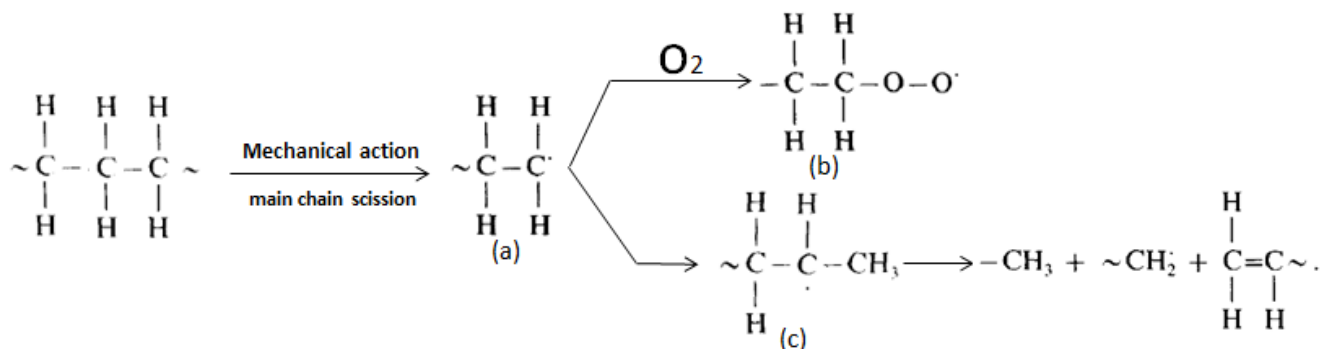


Figure3.1-1. Mechanochemistry of Polyethylene[6]

3.2 Generation mechanism of VOCs

VOCs which may be generated from plastics are hazardous to human health and the environment. Some of these VOCs are produced by chain scissions. There are three kinds of the chain scissions of polymer molecules. One is breaking the chemical bonds in the polymer molecule and which often happens randomly; one is proceeding at the polymer end chains and the initial monomers are broken off which is called depolymerisation; and one is that the side atoms or the groups attached to polymer main chain are released which usually causes volatile molecules; and some of them are produced by the non-polymeric components in the plastic products, such as residual monomers, oligomers, low molecular weight fragments, catalyst remnants, polymerisation solvents and various additives. Because they all have low molecular weight and are weakly bound or not bound at all to the polymeric molecules, they or their degradation products can be emitted from the plastics to air or other media.[3]

3.3 force characteristics of different shapes of plastics

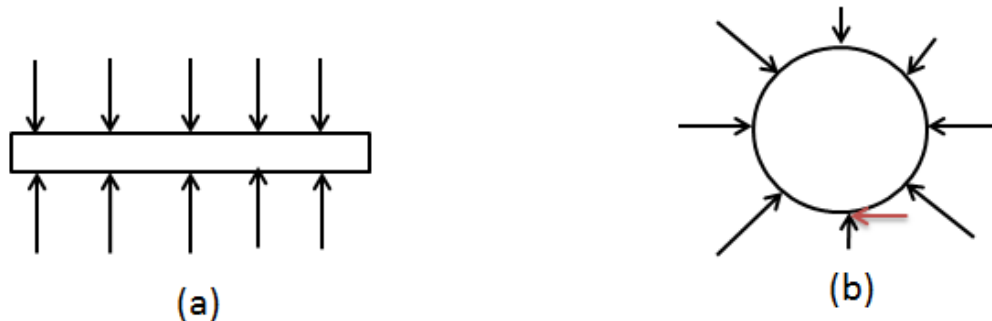


Figure3.3-1. Force analysis(a) sheet; (b) ball

When sheet plastics are used, the force is only the pressures coming from right above and below. However, when ball plastics are used, the force consisting of pressures and frictions can come from any directions.

The strong mechanical action ---friction---always produces large amounts of heat in the system. And the contact area may reach a high temperature in a moment.

3.4 Viscoelastic creep in polymers

Plastic material is one of the viscoelastic materials. When a plastic material is under a constant stress, it will experience a time-dependent increase in strain which is known as viscoelastic creep. As Figure3.4-1 shows, at a time t_0 , a viscoelastic material is loaded with a constant stress that is maintained for a sufficiently long time period. The material responds to the stress with a strain that increases until the material ultimately fails, or may not fail depending on the applied stress versus the material's ultimate resistance. When the stress is maintained for a shorter time period, the material undergoes an initial strain until a time t_1 , after which the strain immediately decreases

(discontinuity) then gradually decreases at times $t > t_1$ to a residual strain.

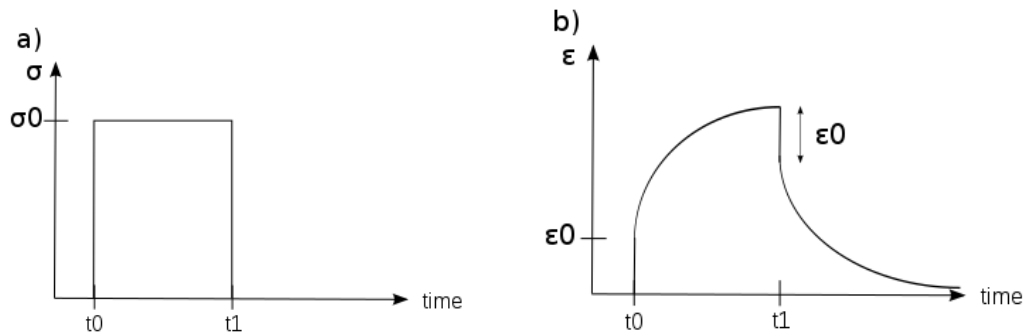
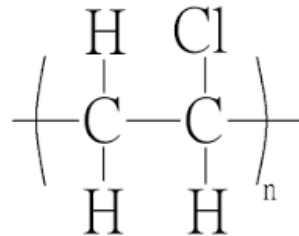


Figure 3.4-1. a) Applied stress and b) induced strain as functions of time for a viscoelastic material[24]

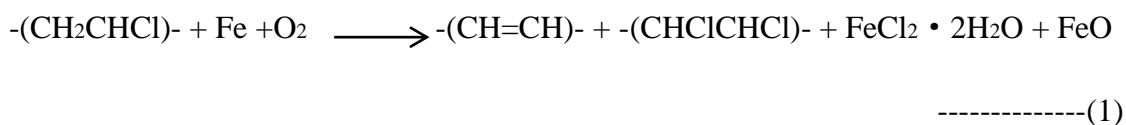
3.5 reaction of PVC with Fe/Al

The chemical structure of PVC is shown as below:



Compared with carbon hydrogen bond (C-H, bond energy is 460 kJ/mol), carbon chlorine bond (C-Cl, bond energy is 326 kJ/mol) has a relatively low bond energy, therefore it has a higher chemical reactivity. And it is polar, the electron pair in the C-Cl bond will be dragged towards the Cl end, leaving the Cl slightly negative (δ^-) and the C slightly positive (δ^+). Hence Cl can react with metals more easily.

Regarding the reaction of PVC with Fe in the air, it can be described as follows[7]:



As for the reaction with Al in the air, the interaction may take place as follows[7]:



According to reactions (1) and (2), the amount of Cl reacting with Fe is two times larger than that with Al, thus the reaction of PVC with Fe is more significant than that of PVC with Al.

3.6 calibration curve

To quantitatively analyze the VOCs produced from the compression, calibration curves of the results of GC are made.

Calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. And it is a plot of how the instrumental response which changes with the concentration of the analyte. By using linear regression analysis, the data-the concentrations of the analyte and the instrument response for each standard-can be fit to a straight line. An equation $y=kx+b$, where y is the instrument response, k represents the sensitivity, and b is a constant. And x which is the analyte concentration of unknown samples can be calculated from this equation.

In this study, a series of standard samples with known concentration and the peak area of the GC results is used to get the equation. Then the concentration of the unknown sample can be calculated once the peak area is known.

4. Experimental

4.1 Main equipments and materials

4.1.1 compression machine

Figure 4.1-1 shows the compression machine used in this experiment which can regulate pressure from 0 to 1MPa. The volume of the container is about 17 L.



Figure4.1-1.Plastics compression machine (丸東製作所 製)

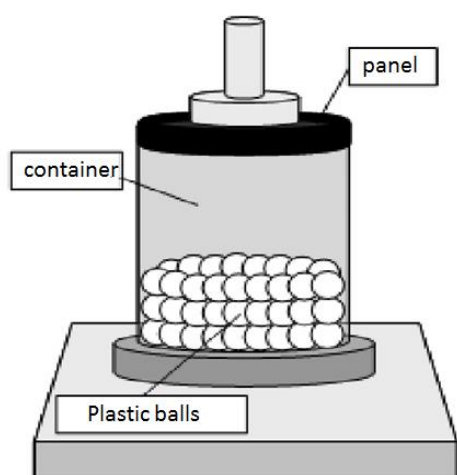


Figure4.1-2. Diagram of the plastics compression machine

4.1.2 Gas Chromatograph (GC)

1)GC-FID

GC-FID is used to analyze VOCs generated by the experiments. Temperature program is shown in Figure 4.1.2-1.

GC: GC-14A (島津製作所 製)

Detector: Flame Ionization Detector

Column: TC-1 (Agilent)

(length: 60.0m, inner diameter: 320 μ m, thickness: 0.25 μ m,
100% dimethylpolysiloxane)

Carrier gas: N₂

Chromatographic pack(data processing equipment): C-R8A (島津製作所 製)

Analysis conditions

Flow rate: 3ml/min

Injector temperature: 200°C

Detector: 200°C

Column oven: temperature program I (Figure4.1.2-1)

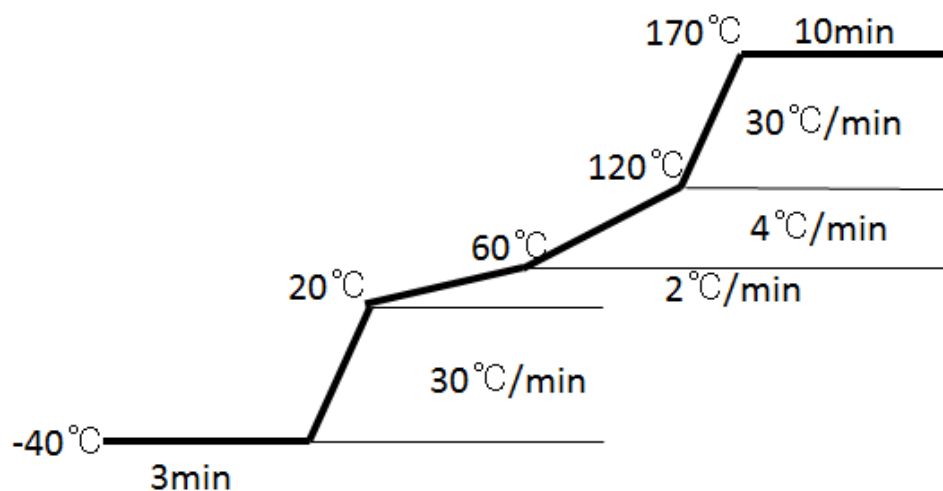


Figure4.1.2-1 temperature program

2) GC-MS

GC-MS is used to identify the products. And the temperature program is the same as that in GC-FID analysis.

GC: GC-17A (島津製作所 製)

Detector: mass spectrometer (GCMS-QP5050)

Column: TC-1 (Agilent)

(length: 60.0m, inner diameter: 320 μ m, thickness: 0.25 μ m,
100% dimethylpolysiloxane)

Carrier gas: He

Analysis conditions

Flow rate: 1ml/min

Column oven: temperature program I (Figure4.1.2-1)

4.1.3 other equipments

1) Sorbent tube

AERO TD GL TUBE TYPE-1 3mm TENAX TA 60/80 100mg(ジーエルサイエンス(株)製)

2) Gas collecting apparatus

MODEI SM-1(サンキュウ技研製)

3) Oven(to clean the sorbent tube)

COLUMN AGING OVEN

KS-5S (GASUKURO KOGYO INC.)

4.1.4 Materials

1)Plastics

Plastic sheet (PE, PP, PVC) (株式会社プラポート製)

Size: 1×50×50mm

Weight: PE---2.53g PP---2.44g PVC---3.58g

Plastic balls (PE,PVC,PP) (旭化成ケミカル社 製)

Diameter: 24mm

Weight: PE---7.88g PP---7.45g PVC---11.45g

2)Metals

Fe balls and Al balls (E-Metals)

Size: 4.7625mm

Fe balls (Quality: SUJ-2; Lot: 2023441; Class: 20)

Al balls (Quality: A1050; Lot: 290410; Class: 1)

Carbon steel balls and Al balls (大橋鋼球株式会社製)

Size: 10mm

Carbon steel balls (Quality: 5N)

Al balls(Quality: SWCH10R)

3) chemical reagents

a) **Toluene**(和光純薬工業株式会社)

Molecular weight: $\text{C}_6\text{H}_5\text{CH}_3=92.14$

Density(20°C): 0.864-0.868g/ml

Assay: 99.5%

b) **Hexane**(和光純薬工業株式会社)

Molecular weight: $\text{CH}_3(\text{CH}_2)_4\text{CH}_3=86.18$

Density(20°C): 0.655-0.660g/ml

Assay: 96.0%

4.2 Methods

4.2.1 Main steps

Group 1 shape comparison

1)sheet PE vs. ball PE;2) sheet PP vs. ball PP; 3) sheet PVC vs. ball PVC

Group2 mixture with PVC

1)sheet PVC+PE, ball PVC+PE; 2)sheet PVC+PP , ball PVC+PP

Group 3 mixture with metals

1)ball PVC+Al ;2)ball PVC+Fe

Experimental Flow Chart

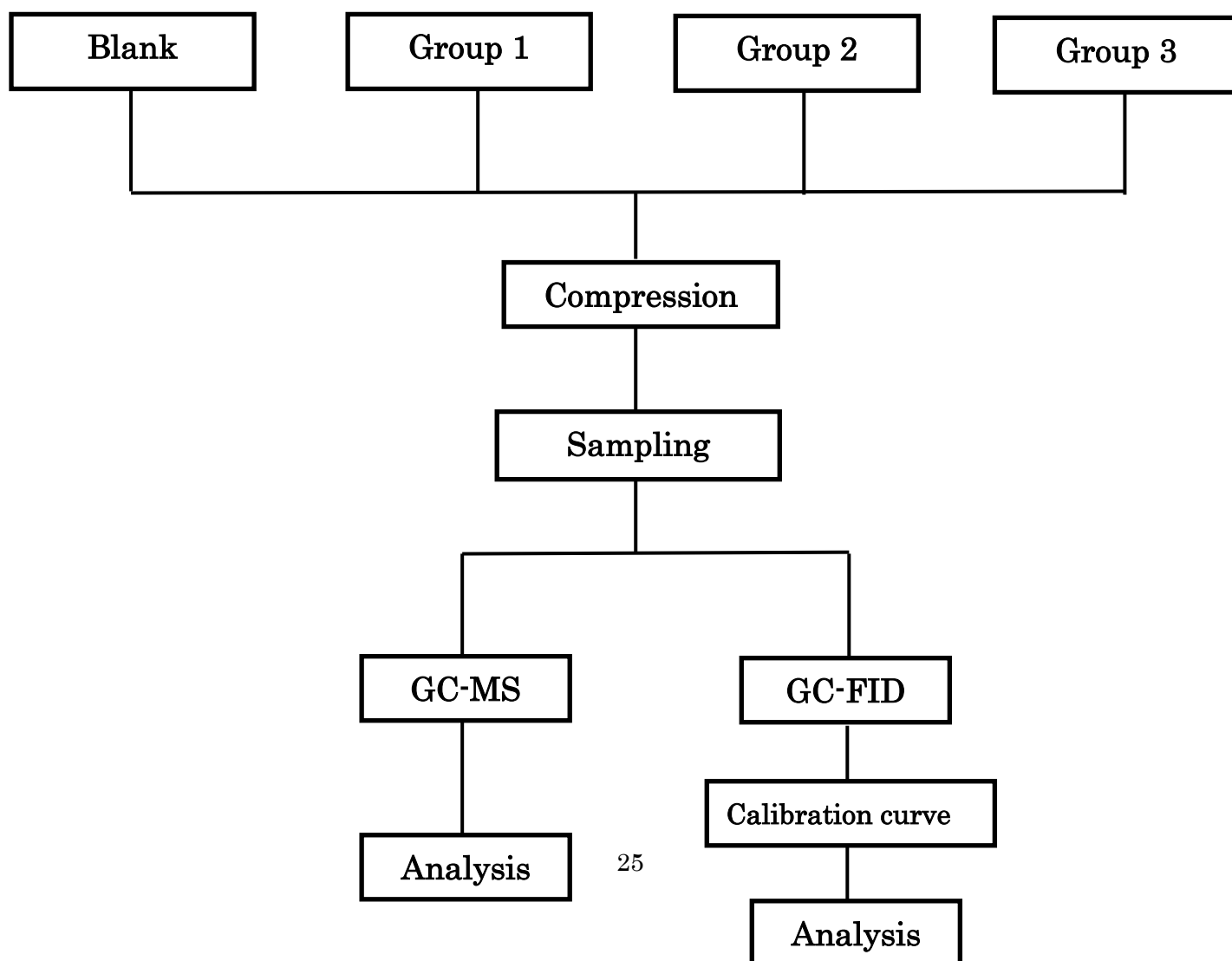




Figure 4.2-1 Equipments (GC, compression machine, compressor, sample injector)

Before taking the sample of VOCs, Tenax tubes have to be cleaned for at least 30min in the column aging oven at the temperature of 200 degrees in the Nitrogen gas atmosphere, then cooled down to room temperature.

For Blank group, pure air is put in the compression machine for 10min (flow rate is about 2 NI/min) to replace the indoor air which has some VOCs and will have negative effects on the results. Compress the pure air, after 10min, use gas collecting apparatus to take the sample, 100ml/min for 10min.

For group1, in each sheet plastics group there are 62 sheets of the plastics, while in each ball plastics group there are 200 balls of the plastics. First put pure air in the compression machine

to replace the indoor air, then compress the plastics for 10min with the pressure 0.36 MPa. Then take the sample.

For group 2, in sheet plastics group, there are 31sheets of PVC and 31sheets of PE or PP; while in ball plastics group, there are 100 balls of PVC and 100 balls of PE or PP. Other steps are the same as that of Group 1.

For group3, in each group, there are 200 balls of PVC and 200 balls of Al or Fe.

Since this experiment has a low repeatability, each group have to be taken at least 5 times.

4.2.2 Additional notes of using GC-FID /GC-MS

- 1) Before using GC-FID, preheat it for about one hour. The column temperature is 200 degree.
- 2)Before starting the analysis of GC-MS, wait until the injector pressure is stable at 100kPa after setting the sample.
- 3) Reset each analysis.

4.2.3 how to make calibration curve

In this study, the standard gas sample is made by a vacuum flask.

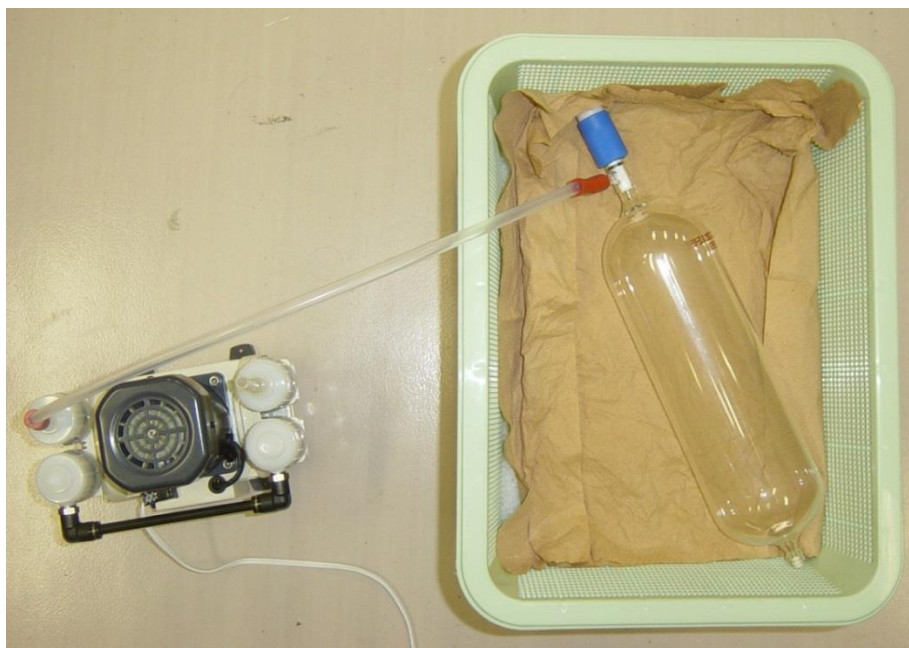


Figure 4.2.3-1 vaccum flask and pump

Vaccum flask: 1009 mL (ジーエルサイエンス 株式会社 製)

Pump: ULVAC DA-15D (ULVAC KINO Inc.)

How to make the standard gas sample:

Use the pump to pump out the air in the vaccum flask. Use microsyringe($10\ \mu\text{L}$) to take the standard chemicals about $1\ \mu\text{L}$, then inject it into the vaccum flask. Let air in the flask. A standard gas sample is done. Use microsyringe(1ml) to take different amount of samples (such as 0.1 mL, 0.15 mL, 0.3 mL, 0.5 mL, 1 mL), then inject it into clean Tenax tube. Use GC-FID to analyze these samples with the same condition with the analysis of VOCs generated during the compression of plastics.

Use the peak areas and different amounts of standard chemical sample to make the calibration curve. Then use the curve to calculate the amount of the certain

chemical generated during the compression of plasitics.

5. Results and Discussions

5.1 Results of GC-MS

5.1.1 GC-MS of VOCs in the air

Table 5.1.1-1 shows the VOCs in the air and its retention time.

Table 5.1.1-1. Chemicals and its retention time in the air

Retention time/min	chemicals	Retention time/min	chemicals	Retention time/min	chemicals
4.435	propane	10.010	Methyl-cyclopentane	21.872	Ethylbenzene
4.568	Chloromethane	10.979	Benzene	22.289	p-xylene
4.704	Isotubane	11.387	Cyclohexane	23.143	Styrene
4.985	Butane	11.901	Pentanal	23.395	1,3-dimethyl benzene
5.490	ethanol	12.580	Trichloroethylene	25.325	Benzaldehyde
5.196	Acetone	12.997	Acetic acid	26.770	Octanal
6.440	1,3-butadiene	13.075	Heptane	27.246	Decane
7.100	Carbon disulfide	16.256	Toluene-d8	27.343	Dichloro-benzene
7.992	2-methyl-pentane	16.489	Toluene	27.605	2-ethy-1-hexanal
8.225	2-butanone	17.662	Hexanal	29.457	Nonanal
8.428	3-methyl-pentane	18.953	Octane	31.911	Decanal
8.952	Hexane	20.892	Chloro-benzene	32.134	dodecane

5.1.2 GC-MS results of the compression of PE

Table 5.1.2-1 shows results of the compression of PE.

Table 5.1.2-1 GC-MS results of the compression of PE

Retention time/min	Chemicals	Retention time/min	Chemicals	Retention time/min	Chemicals
4.025	CO2	10.951	benzene	23.521	1-octanol
4.316	carbonyl sulfide	11.377	cyclohexane	23.977	nonane
4.685	acetaldehyde	11.872	pentanal	25.316	benzaldehyde
4.859	2-methyl-propene	16.227	toluene-d8	26.451	3-methyl-nonane
4.956	butane	16.470	toluene	26.761	octanal
5.432	ethanol	17.440	3-methyl-heptane	26.945	trimethyl-benzene
5.849	acetone	17.643	hexanal	27.236	decane
6.062	isopropyl alcohol	18.283	1-octene	27.333	dichloro-benzene
7.051	1-propanethiol	18.953	octane	27.595	2-ethyl-1-hexanal
7.983	2-methyl-pentane	20.883	chloro-benzene	29.448	nonanal
8.060	butanal	21.863	ethylbenzene	29.787	undecane
8.177	2-butanone	22.280	p-xylene	31.494	3-methyl-undecane
8.409	3-methyl-pentane	22.503	3-heptanone	31.892	decanal
8.943	hexane	22.639	cyclohexanone	32.125	dodecane
10.000	methyl-cyclopentane	23.143	styrene	34.676	tridecane

10.844	1-butanol	23.366	1,3-dimethyl-benzene
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When ball plastics are compressed, a huge pressure is always accompanied by friction which produces large amounts of heat in the system. It may cause a high temperature in one moment. Therefore, the VOCs might be postulated as thermally caused.

Hence to figure out it is the mechanical action that generated some new VOCs, the results of the compression of PE is compared with the VOCs products of thermal degradation of PE_[9]. Table 5.1.2-2. Chemicals in red are the chemicals which do not shown in the thermal degradation products of PE. This illustrates that the mechanism in the compression is different from that in thermal degradation. Some VOCs do result from the compression.

Table 5.1.2-2. comparison of the compression products with thermal degradation products of PE

Thermal degradation products (pyrolysis, thermos-oxidation, combustion)	Compression of PE
Carbon dioxide	Carbon dioxide
Propylene	Carbonyl sulfide
butylene	acetaldehyde
Butane	2-methyl-propene
1,2-butadiene	Butane
Pentene+propanal	ethanol
n-pentane	acetone
C ₅ H ₈	isopropyl alcohol
C ₅ H ₁₀	1-propanethiol

Butyraldehyde	2-methyl-pentane
Cyclohexane	butanal
Hexane-1	2-butanone
n-hexane	3-methyl-pentane
C ₆ H ₁₄	hexane
C ₆ H ₁₀	methyl-cyclopentane
Cyclohexene	1-butanol
Benzene	benzene
Methylcyclopentene	cyclohexane
Varelaldehyde	pentanal
Heptane-1	toluene-d8
n-heptene	toluene
C ₇ H ₁₄	3-methyl-heptane
Toluene	hexanal
Ethylcyclopentene	1-octene
Methyl isobutyl ketone(allyl acetate)	octane
Hexanal	chlorobenzene
Octen-1	ethylbenzene
n-octane	p-xylene
C ₈ H ₁₈	3-heptanone
Acrylic acid	cyclohexanone
Ethyl benzene	styrene
C ₉ H ₁₈	1,3-dimethyl-benzene
Heptanal	1-octanol
Nonene-1	nonane
n-Nonane	benzaldehyde
C ₉ H ₁₆	3-methyl-nonane
Keto-aldehyde	octanal
Octanal	trimethyl-benzene
Decene-1	decane
n-Decane	dichloro-benzene
C ₁₀ H ₁₈	2-ethyl-1-hexanal
C ₁₀ H ₂₀	nonanal
C ₁₀ H ₂₂	undecane

Undecene-1	3-methyl-undecane
n-Undecane	decanal
Nonanal	dodecane
C₁₁H₂₄	tridecane
C₁₁H₂₀	
Dodecene-1	
n-Dodecane	
Decanal	
n-Tridecane	
undecanal	
C₁₃H₂₆	
Silicone	
Tetradecene-1	
n-Tetradecane	
Dodecanal	
Pentadecene-1	
n-Pentadecane	
Tridecanal	
Hexadecene-1	
Tetradecanal	
Heptadecene-1+n-Heptadecane	
Pentadecanal	
Octadecene-1+n-Octadecane	

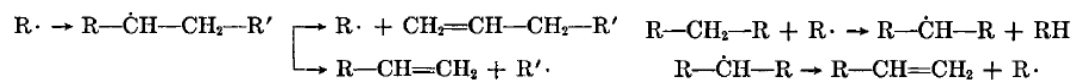
According to table 5.1.2-2, there are many alkenes in the thermal products, however, they nearly can't be found in the compression products. On the contrary, there are alcohols in the compression products while they are not found in the thermal products.

The mechanism of thermal degradation of PE can be explained as follows, where R is a macromolecule and R' is a small n-alkane group:[21]

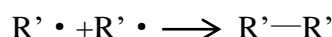
Initiation: $R-R \longrightarrow 2R \cdot$

Propagation: $R \cdot \longrightarrow R \cdot + CH_2=CH_2$

Intermolecular transfer followed by a decomposition reaction



Termination: $R' \cdot + R' \cdot \longrightarrow R'-CH=CH_2 + R'H$



The free radicals result from the main chain scissions of preferential scission of weak bonds caused by irregularities in the polymer chain and of random scission of ordinary C-C bonds. The weak bonds may be due to the presence of oxygen, or to the presence of double bonds in the chain, which results in weaker bonds in the β position to the double bonds, or to branching. According to Koseki's research, [17] after the compression, there is nearly no change in the average molecular weight and molecular weight distribution, hence the possibility of a main chain scission is low. Maybe the free radicals of compression results from some side chains.

And the reason why there are nearly no alcohol in the thermal degradation products maybe that thermal degradation reacts more thoroughly, thus even there are some alcohols generated, they can be oxidized by oxygen with a high temperature.

5.1.3 GC-MS results of the compression of PP

Table 5.1.3-1 shows results of the compression of PP.

Table 5.1.3-1 GC-MS results of the compression of PP

Retention	chemicals	Retention	chemicals
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time/min		time/min	
4.125	Methyl Alcohol+Acetaldehyde	17.706	Phenol
5.835	Acetonitrile	19.003	2-ethyl- 1-Hexanol
6.190	Acetone	19.167	2,5,5-trimethyl- Heptane
7.941	Carbon disulfide	19.895	5-ethyl-2-methyl- Octane
8.712	2-methyl-pentane	20.388	Nonanal
9.511	Hexane	20.649	5-ethyl-2-methyl-octane
13.751	Toluene	22.166	Decanal
15.062	2,4-dimethyl-heptane	23.247	isothiocyanato-cyclohexane
15.343	N,N-dimethyl-Acetamide	23.701	3,7-dimethyl-Undecane
15.937	4-methyl-octane		

The results of the compression of PP are compared with the thermal degradation products of PP_[9] to determine whether the VOCs here are produced by compression or not. In Table 5.1.3-2, different chemicals are marked in red.

Table.5.1.3-2 comparison of the compression products with thermal degradation products of PP

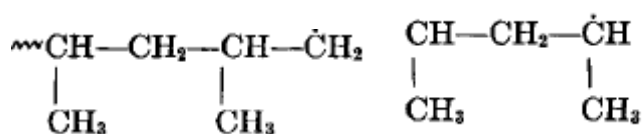
Thermal degradation products (pyrolysis, thermos-oxidation, combustion)	Compression of PP
Carbon dioxide	Methyl Alcohol
Propylene	Acetaldehyde
Acetone	Acetonitrile
n-pentane	Acetone

Cyclopentadiene+acrolein	Carbon disulfide
Hexane	2-methyl-pentane
Crotonaldehyde	Hexane
Dimethylpentadiene	Toluene
2-methyl-1-pentene	2,4-dimethyl-heptane
Acetic acid	N,N-dimethyl- Acetamide
C ₈ H ₁₆	4-methyl-octane
2-butylene-1-ol	Phenol
1-butanol	2-ethyl- 1-Hexanol
C ₈ H ₁₈	2,5,5-trimethyl- Heptane
Diacetyl	5-ethyl-2-methyl- Octane
C ₈ H ₁₄	Nonanal
4-methyl-2-pentanone	5-ethyl-2-methyl-octane
C ₆ H ₁₂ CO Ketone	Decanal
Toluene	isothiocyanato-cyclohexane
C ₉ H ₁₈	3,7-dimethyl- Undecane
C ₉ H ₂₀	
Acetyl acetone	
C ₇ H ₁₄ CO Ketone	
2-Heptanone	
2,6-dimethyl-3-heptene	
Epoxide	
C ₉ H ₁₆	
C ₁₀ H ₂₀	
C ₁₀ H ₁₈	
4-methyl-2-heptanone	
Ketone or epoxide	
C ₉ H ₁₆ O Ketone	
C ₁₁ H ₂₂	
4,6-Dimethyl nonane	
C ₉ H ₁₈ O ketone	
C ₁₂ H ₂₄ mixture	
C ₁₃ H ₂₆	
C ₁₃ H ₂₄	

C ₁₄ H ₂₈
C ₁₄ H ₂₆
C ₁₂ H ₂₂ O Ketone
C ₁₅ H ₃₀
C ₁₅ H ₂₈
C ₁₄ H ₂₆ O Ketone
C ₁₅ H ₂₈ O Ketone
C ₁₈ H ₃₆

According to Table5.1.3-1 and Table5.1.3-2, though there are less types of VOCs generated during the compression of PP compared with those generated during the compression of PE which maybe because the chemical structure of PP is more stable than PE, most of these VOCs are different from the thermal degradation products of PP. And in the same as the results of PE, there are no alkenes in the compression products which are found in thermal products; while there are nearly no alcohols in the thermal degradation products which are found in compression products.

The initiation reaction occurs by random scission of main chain, yielding two types of radicals: primary and secondary. [22]



1)primary radicals

2)secondary radicals

The difference of products maybe the same reason as that of PE. Free radicals generated by the compression result from side chain scissions or side group scissions instead of main chain scissions. And thermal degradation can react more thoroughly than mechanochemical reaction.

5.1.4 GC-MS results of the compression of PVC

Table 5.1.4-1 shows results of the compression of PVC.

Table 5.1.4-1 GC-MS results of the compression of PVC

Retention time/min	Chemicals	Retention time/min	Chemicals	Retention time/min	Chemicals
3.080	formaldehyde	8.850	2-butanone	16.574	strene
3.311	sulfur dioxide	9.358	ethyl acetate	16.726	o-xylene
3.417	carbonyl sulfide	9.505	hexane	17.704	phenol
4.157	methyl alcohol	10.033	tetrahydro-furan	18.303	2,5-dimethyl-heptane
4.536	2-methyl-1-propene	10.643	1-butanol	18.455	octanal
4.612	(Z)-2-butene	11.092	benzene	18.664	decane
5.427	ethyl alcohol	12.236	formic acid, butyl ester	18.802	1,2,4-trimethyl-benzene
5.832	methyl isocyanide	13.754	toluene	18.996	2-ethyl-1-hexanol
6.186	acetone	14.034	hexanal	19.158	2,5,5-trimethyl-heptane
6.417	isopropyl alcohol	15.056	2,4-dimethyl-heptane	19.890	5-ethyl-2-methyl-octane
6.642	formic acid	15.344	N,N-dimethyl-acetamide	20.017	2-methyl-undecane
7.406	1,3-dichloro-2-propanol	15.943	hexane, 2,3,4-trimethyl- +	20.383	nonanal

ethylbenzene					
7.939	carbon disulfide	16.124	p-xylene	20.508	undecane
8.164	acetic acid	16.333	heptanal	20.647	6-ethyl-2-methyl-octane
8.771	butanal	16.447	cyclohexanone	23.238	isothiocyanato-cyclohexane

The results of the compression of PVC are compared with the thermal degradation products of PP_[10] to determine whether the VOCs here are produced by compression or not. In Table 5.1.4-2, different chemicals are marked in red.

Table 5.1.4-2 comparison of the compression products with thermal degradation products of PVC

Thermal degradation products (pyrolysis, combustion)	Chemicals
Carbon dioxide	formaldehyde
Chloromethane	sulfur dioxide
Cyclopentane	carbonyl sulfide
Cyclopentadiene	methyl alcohol
Cyclohexadiene	2-methyl-1-propene
Benzene	(Z)-2-butene
Toluene	ethyl alcohol
Dioxane	methyl isocyanide
Xylene	acetone
Styrene	isopropyl alcohol
Methyl styrene	formic acid
Indene	1,3-dichloro-2-propanol
Naphthalene	carbon disulfide

Butadiene	acetic acid
Vinyl chloride	butanal
Acetaldehyde	2-butanone
Methylcyclopentene	ethyl acetate
Chlorobenzene	hexane
Divinylbenzene	tetrahydro-furan
Cyclopentene	1-butanol
Trichloroethylene	benzene
Chloroethane	formic acid, butyl ester
Chloropropene	toluene
Propanal	hexanal
Methyl ethyl cyclopentane	2,4-dimethyl-heptane
Trimethylcyclopentane	N,N-dimethyl-acetamide
Methyl cyclohexene	hexane, 2,3,4-trimethyl- + ethylbenzene
Methyl indane	p-xylene
Cyclohexene	heptanal
Trimethylbenzene	cyclohexanone
Dichloroethylene	styrene
Acrylonitrile	o-xylene
Hydrogen cyanide	phenol
Acetonitrile	2,5-dimethyl-heptane
Dichlorobutadiene	octanal
Dichloropentene	decane
Trichloropropane	1,2,4-trimethyl-benzene
Dichlorobenzene	2-ethyl-1-hexanol
Trichlorobenzene	2,5,5-trimethyl-heptane
p-Chlorobenzonitrile	5-ethyl-2-methyl-octane
Dichlorobenzonitrile	2-methyl-undecane
Dichloropropene	nonanal
Methylmethacrylate	undecane
Trimethylpentene	6-ethyl-2-methyl-octane
Dichlorobutylene	isothiocyanato-cyclohexane
dichloropentadiene	
Dichlorocyclopentene	

Benzaldehyde
Trichlorobutylene
Chloropyridine
n-propylbenzene
Chlorobenzonitrile
Dichlorotoluene
p-Dichlorobenzonitrile
Methylnaphthalene
Chloronaphthalene
Chlorostyrene
Diphenyl
Tetradecylene
Pentadecylene
Dichloroethylbenzene
Diphenylethane
di-tert-butyl methyl phenol
Hexadecylene
Diphenylbutylene
Hydrogen chloride

According to Table 5.1.4-2, the types of the thermal degradation products of PVC are more than that of the compression of PVC. And most of them are different from each other. And like the results of PE and PP, there are nearly no alkenes in compression products which are found in thermal degradation products; while there are nearly no alcohols in thermal degradation products which are found in compression products.

The initiation free radicals of the thermal degradation result from the chain scission of the side atoms because C-Cl bond β to a double bond is one of the weakest in the chain and therefore susceptible to attack. The chlorine radical is free to react with another polymer chain or another portion of the same chain, abstracting hydrogen

and forming volatile HCl. As a result, a labile chlorine is produced on the carbon α to the radical position, and subsequently is removed as a chlorine radical. A double bond with an α -methylenic group that is subject to further attack by a chlorine radical is thus formed.[23]

Generally, 1) most of the compression products are different from the thermal degradation products; 2) Numbers of thermal degradation products are more than that of compression products; 3) Many thermal degradation products has a long carbon chain, while compression products are smaller molecules; 4) There are always alkenes in the thermal degradation products, while there is no alkenes in the compression products. However, there are always alcohols in compression products which nearly can't found in the thermal degradation products. These 4 points show that the mechanism of thermal degradation and compression is different. The initiation free radicals of the compression maybe result from chain scission of side groups or side atoms rather than main chain scissions. And thermal degradation can react more thoroughly thus there are nearly no alcohol in its products.

5.2 Calibration curve

Calibration curves for toluene and hexane are shown in Figure 5.2-1 and Figure 5.2.2 where linear correlations are obtained.

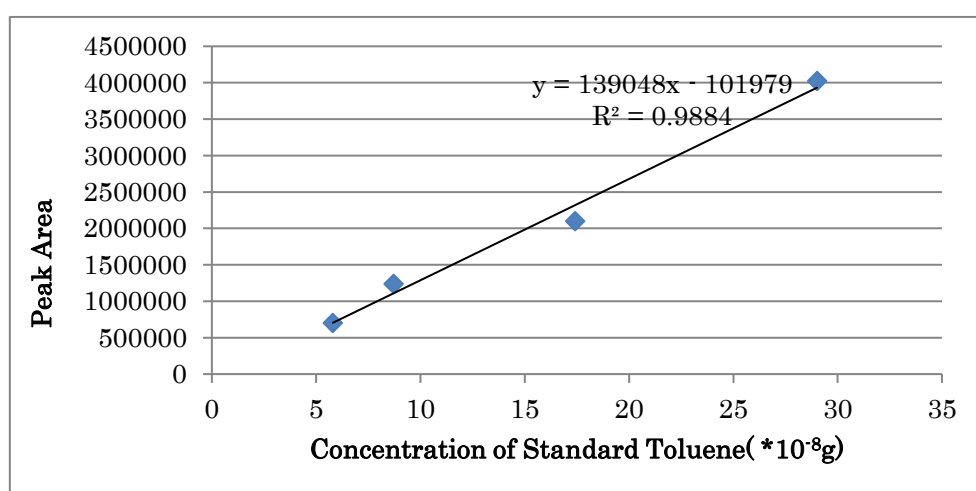


Figure5.2-1. Calibration curve of Toluene

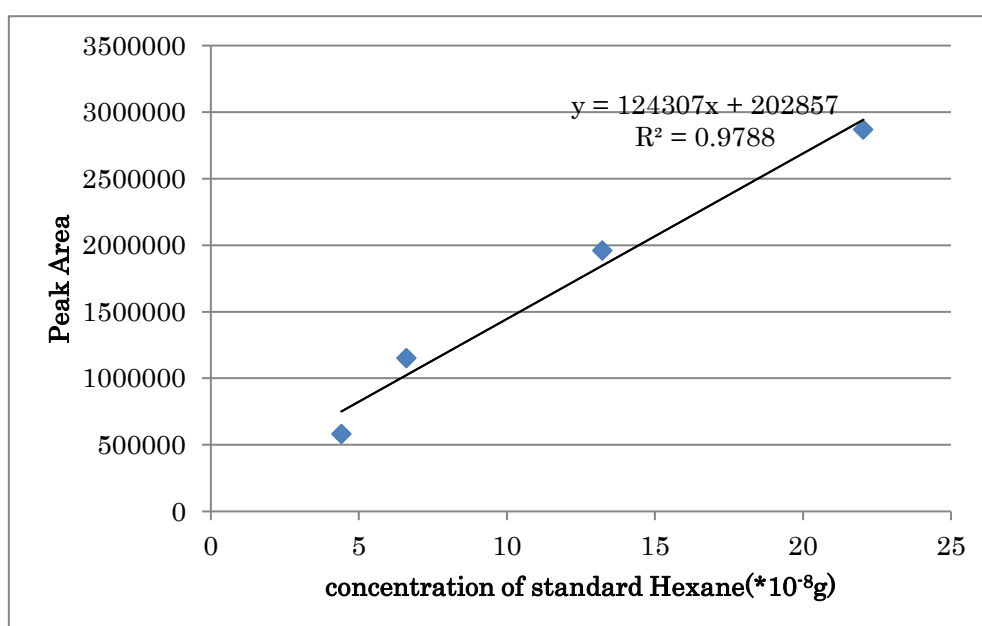


Figure 5.2.2 calibration curve of Hexane

5.3 Results of GC-FID

5.3.1 Blank

Here are the GC-FID chromatograms of the pure air which is compressed in the compression machine without any plastics and of the air which is in the air tank. (Figure 5.3.1-1)

In Figure 5.3.1-1, when the retention time is 6.869min, there is a high peak corresponding to acetone which is used to clean the container of the compression machine. According to Figure 5.3.1-1, the main chemicals (peaks 1,2,3,4,5,6) in the air are listed in Table 5.3.1-1. This experiment has a low repeatability, every time the amount of VOCs is different.

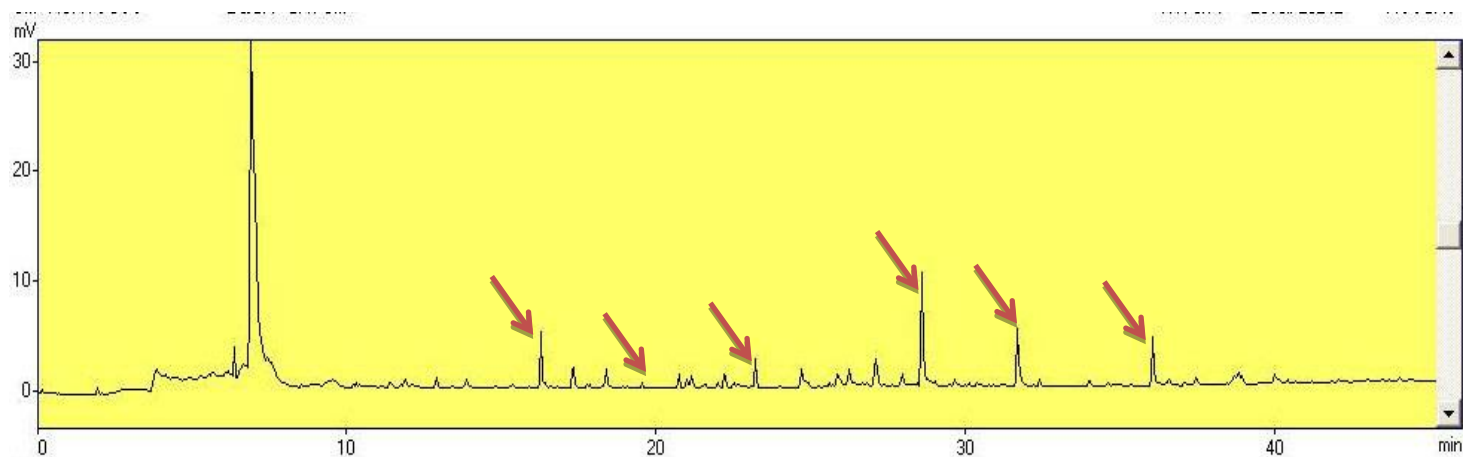
Table 5.3.1-1 main chemicals' retention time and average peak area (n=5, relative error (RE) * is in blue font)

No.	Retention time/min	Average Peak area (n=5)
1	16.205(toluene)	41602/0.30(20219)
2	20.909	28307/0.03(145527)
3	24.657	44131/0.27
4	28.548	92385/0.09
5	31.664	54741/0.11
6	36.008	44570/0.22

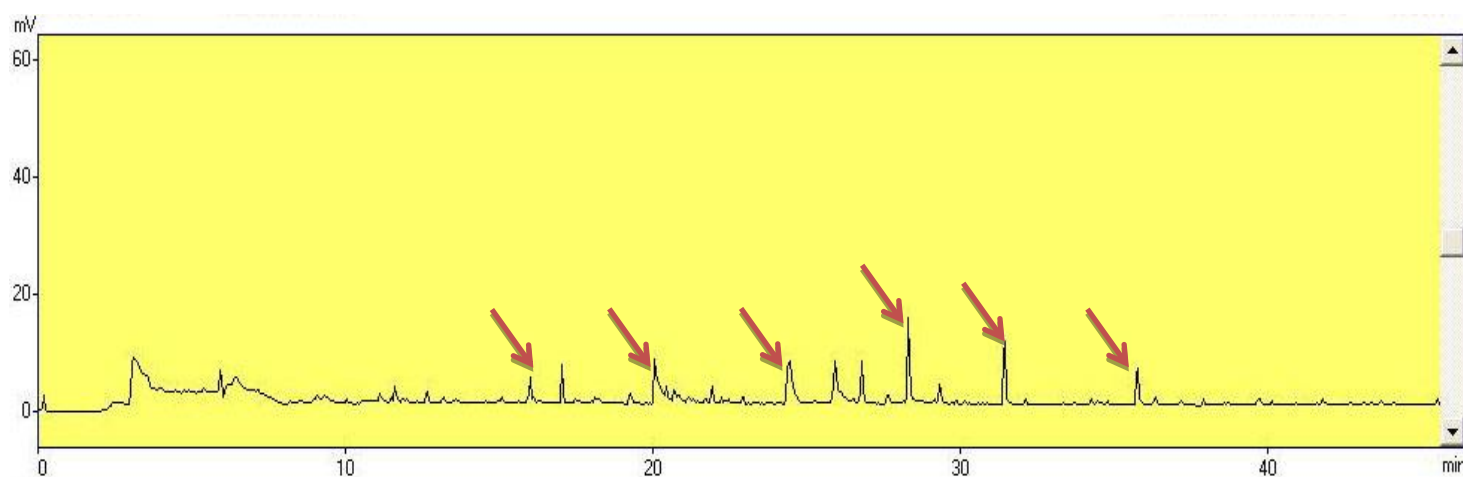
*Relative Error: it is a measure that is used to quantify the amount of variation or dispersion of a set of data values.

By reference to the results of GC-MS, when the retention time is 16.205min, the peak¹ corresponds to Toluene; while the peak² of retention time 20.909 min may be chlorobenzene or ethylbenzene; the peak ⁵ might be decanal.

It is interesting to note that when in the pure air in the tank, according to the results, the peak area of toluene is at most 20219 (according to the calibration curve, the concentration of toluene in the pure air is $1.45 \mu\text{g}/\text{m}^3$ while in the air, the concentration range of toluene is about $0.23\text{--}750 \mu\text{g}/\text{m}^3$ [11]) which means that the amount of toluene in the air is less than that in the compression machine. It is supposed that some VOCs may have been adsorbed on the surface of the compression machine; While at the retention time 20.909min, the peak area of the chemical in the pure air in the tank is over 80000 and the maximum is 145527 which is nearly 5 times that in the compression which means the amount of chemical 2 of the air in the air tank is more than that in the compression. Maybe the chemicals on the surface of the compression machine have reacted with it in the air.



(a)



(b)

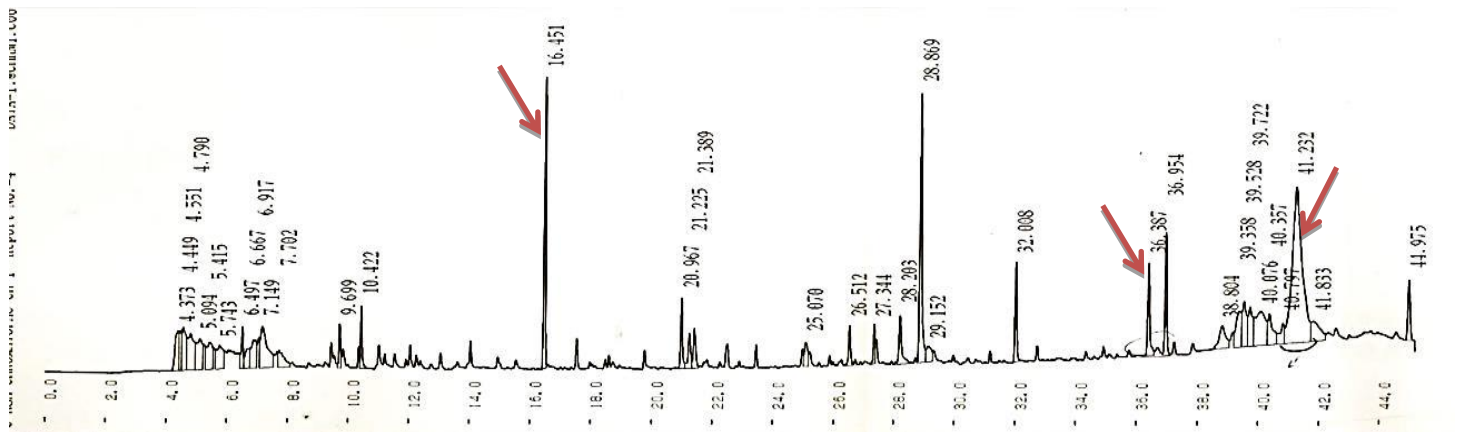
(X: retention time/min; Y: signal intensity/mV)

Figure.5.3.1-1 Chromatograms of (a)VOCs of the pure air in the compression

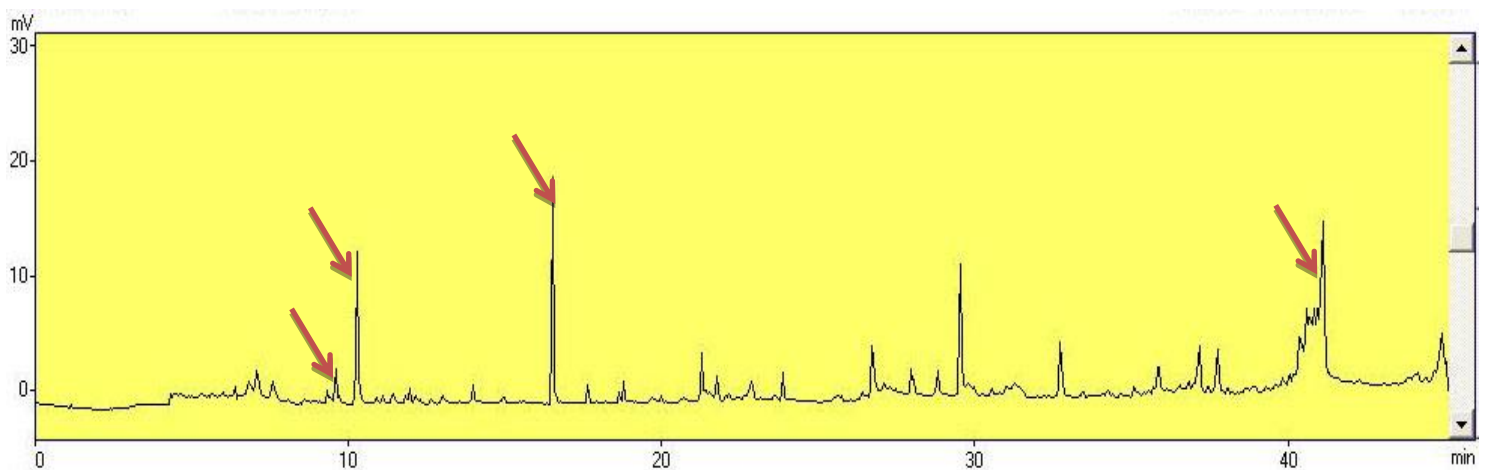
machine (b)VOCs of the pure air in the air tank.

5.3.2 Comparison of sheet plastics with ball plastics (Shape)

1) SheetPE vs Ball PE



(a)



(b)

(X: retention time/min; Y: signal intensity/mV)

Figure5.3.2-1 Chromatograms of (a)VOCs generated during the compression of sheet PE(b)VOCs generated during the compression of ball PE

Based on the results of the **Blank** group, VOCs produced during the compression are listed in Table 5.3.2-1. Main new chemicals are in red.

Table 5.3.2-1 Main chemicals' retention time and average peak area(n=5, relative error(RE) is in blue font)

(a)sheet PE

No.	Retention time	Average Peak area(n=5)
1	16.451	63947/0.30
2	36.954	61486/0.28
3	40.343	142507/0.10

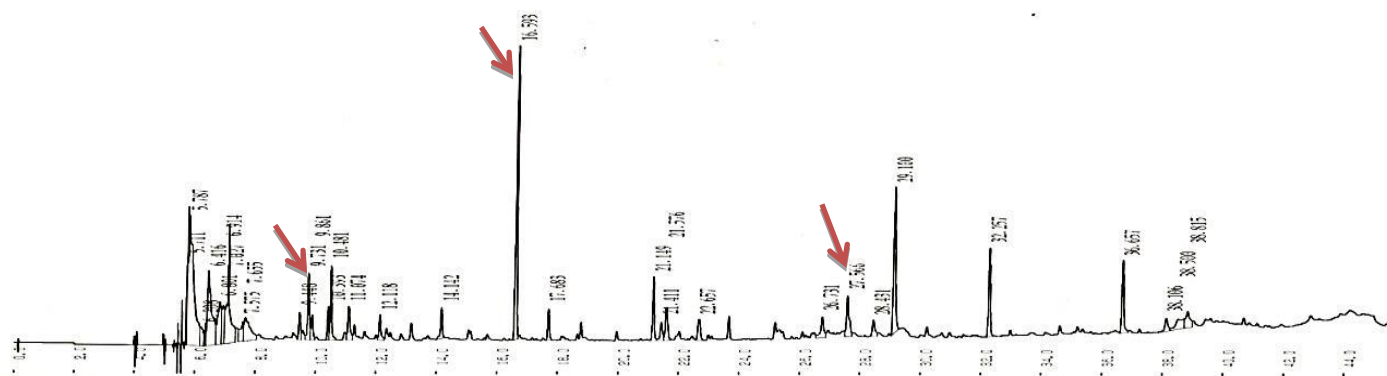
(b)ball PE

No.	Retention time	Average Peak area (n=5)
1'	9.53	23143/0.29
2'	10.26	42106/0.05
3'	16.493	98279/0.26
4'	41.103	110473/0.17

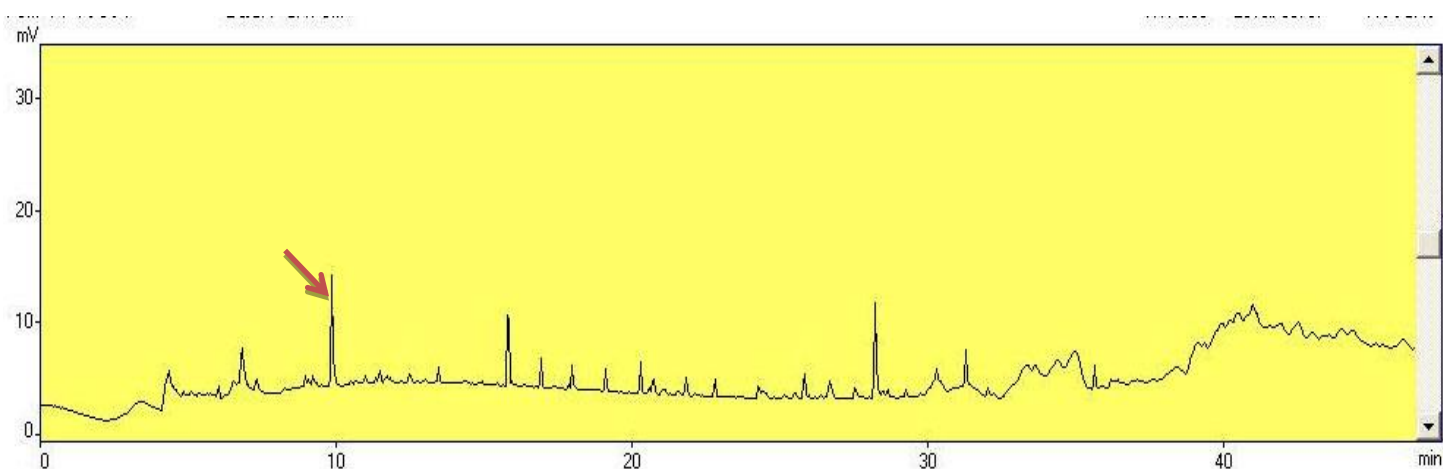
According to Figure5.3.2-1 and Table5.3.2-1, during the compression, sheet PE emits two new kinds of VOCs which are of the retention time 36.954min and 40.343min, respectively; while ball PE emits three new kinds of VOCs at the retention time of 9.53min which might be hexane, 10.26min and 41.103min.

And both during the compression of sheet PE and ball PE, toluene is generated. Based on the calibration curve of toluene, 154.33g sheet PE emitted about 0.161×10^{-8} g toluene, while 1576 g ball PE emitted about 0.408×10^{-8} g toluene. It can be calculated that if samples are of the same weight, sheet PE will emit more toluene than ball PE when they are compressed. This is probably because sheet PE has more contact area during the compression.

2)Sheet PP vs ball PP



(a)



(b)

(X: retention time/min; Y: signal intensity/mV)

Figure5.3.2-2Chromatograms of (a)VOCs generated during the compression of sheet PP(b)VOCs generated during the compression of ball PP

Based on the results of the **Blank** group, VOCs produced during the compression

are listed as in Table 5.3.2-2. Main new chemicals are in red. When retention time is about 10min, the new chemical is probably hexane.

Table 5.3.2-2 Main chemicals' retention time and average peak area(n=5, relative error(RE)*is in blue font)

(a)sheet PP

No.	Retention time/min	Average Peak area
1	10.481	26231/0.33
2	16.593	85951/0.20
3	29.100	99948/0.25

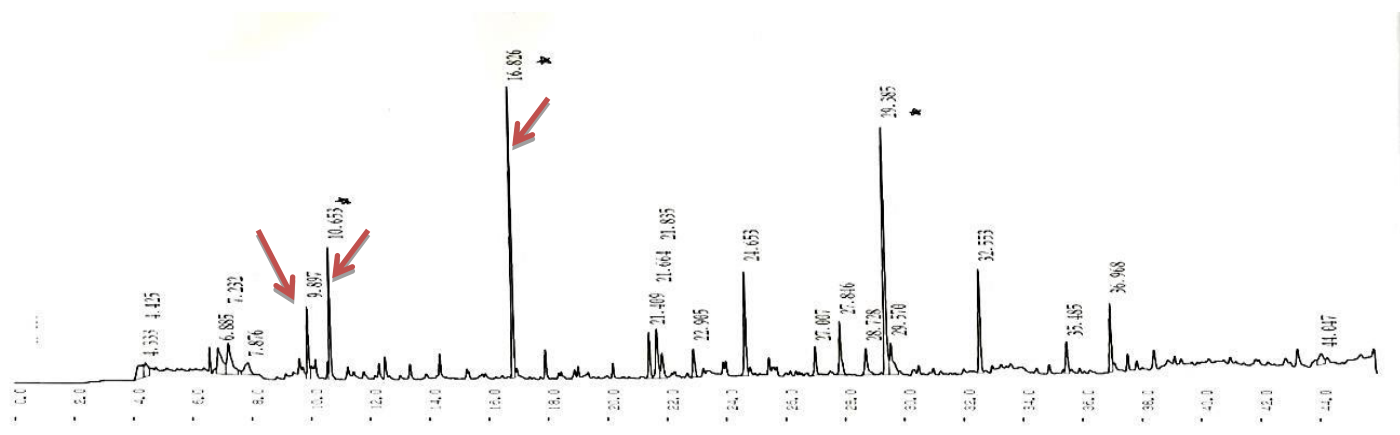
(b)ball PP

No.	Retention time/min	Average Peak area
1'	9.796	33221/0.15

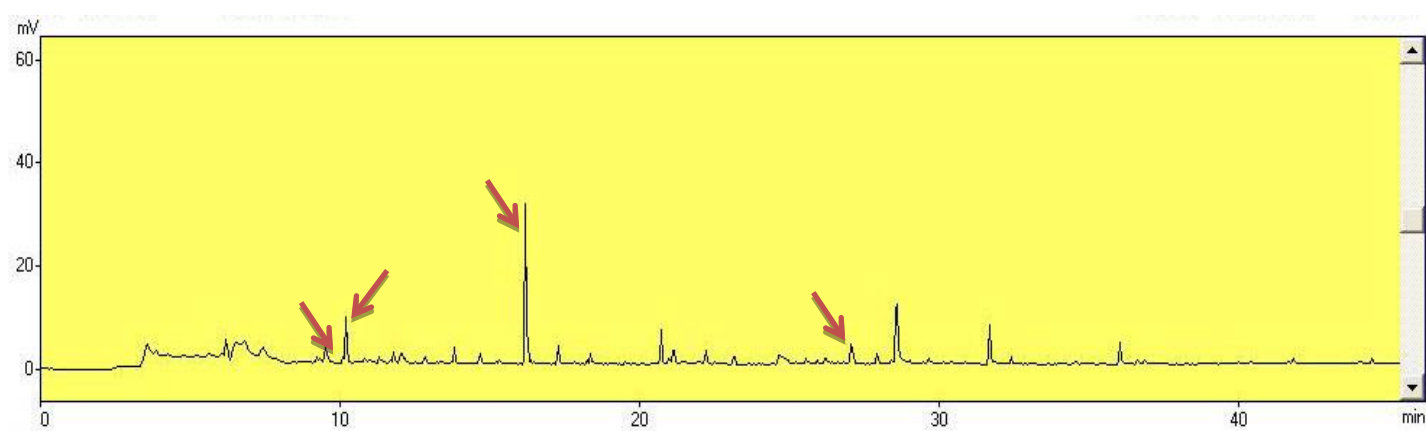
From the chromatograms, it can be seen that sheet PP emits more VOCs than ball PP. There are two possible reasons. One is that sheet PP has more contact area and the other one is that sheet PP is transparent, so it is atactic polypropylene which usually does not crystallize, while ball PP is opaque, it is isotactic polypropylene which usually has crystallinity of about 50%. Crystalline polymer is assumed to be more difficult to generate VOCs under the compression since it has a more regular molecular arrangement than amorphous polymers.

And generally during the compression of PP, less VOCs will be generated than that generated during the compression of PE or PVC. This might also result from its stable chemical structure.

3) Sheet PVC vs ball PVC



(a)



(b)

Figure 5.3.2-3 Chromatograms of (a) VOCs generated during the compression of sheet PVC (b) VOCs generated during the compression of ball PVC

Based on the results of the **Blank** group, VOCs produced during the compression are listed in table 5.3.2-1. Main new chemicals are in red.

Table 5.3.2-1 Main chemicals' retention time and average peak area(n=5, relative error(RE)*is in blue font)

(a)sheet PVC

No.	Retention time	Average Peak area(n=5)
1	9.872	18716/0.22
2	10.634	32950/0.19
3	16.823	79992/0.16

(b)ball PVC

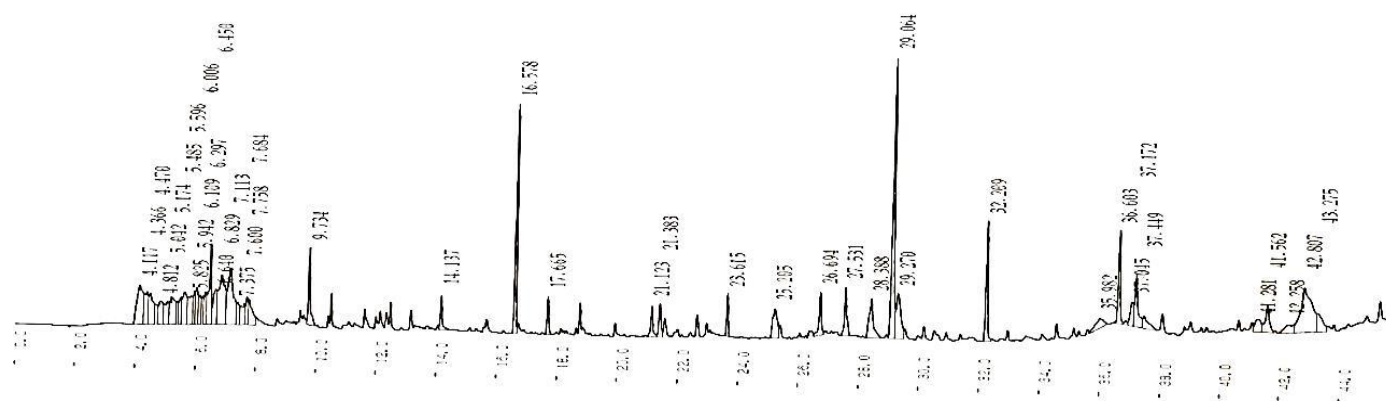
No.	Retention time	Average Peak area(n=5)
1	9.231	24056/0.03
2	9.957	76813/0.36
3	15.919	150623/0.27
4	26.789	34262/0.26

The table shows that both sheet PVC and ball PVC will generate hexane and toluene during the compression. And compared with PP and PE, PVC generates most toluene, about 2290g PVC will generate 1.08×10^{-8} g toluene.

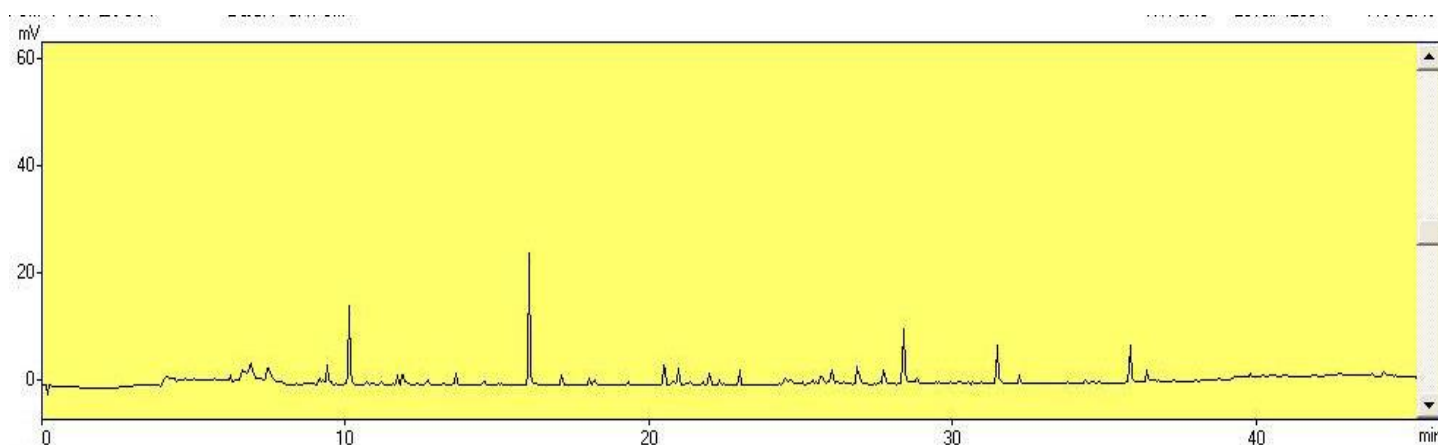
Compared with sheet PVC, ball PVC has generated one more new chemical of the retention time 26.789min.

In summary, sheet plastics will generate more VOCs than ball plastics when they are of the same weight because sheet plastics have more contact area. However, apart from ball PP which has a crystallinity of about 50% and is difficult to react during the compression, ball plastics will usually generate more types of VOCs. It might be because not only compression but also friction exists during the compression of ball plastics.

1)PVC+PE



(a)Sheet

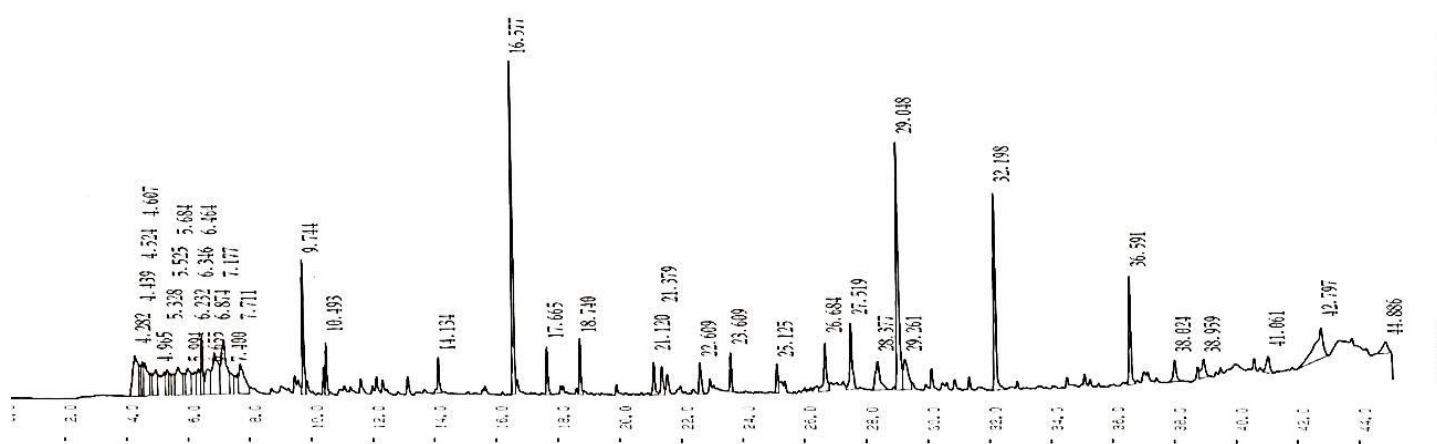


(b)Ball

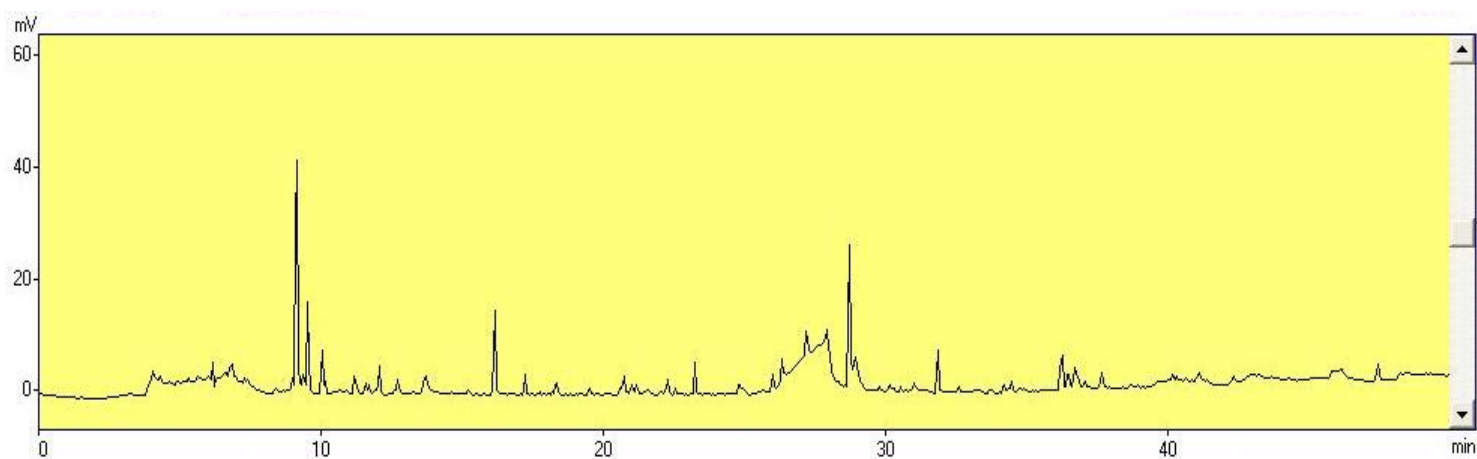
Figure 5.3.3-1. Chromatograms of (a) VOCs generated during the compression of sheet PVC+PE (b) VOCs generated during the compression of ball PVC+PE

There are no new chemicals and all the peak areas are almost the same as that of the compression of PE, PP, PVC, respectively.

2)PVC+PP



(a) sheet



(b) ball

Figure5.3.3-2.Chromatograms of (a)VOCs generated during the compression of sheet PVC+PP(b)VOCs generated during the compression of ball PVC+PP

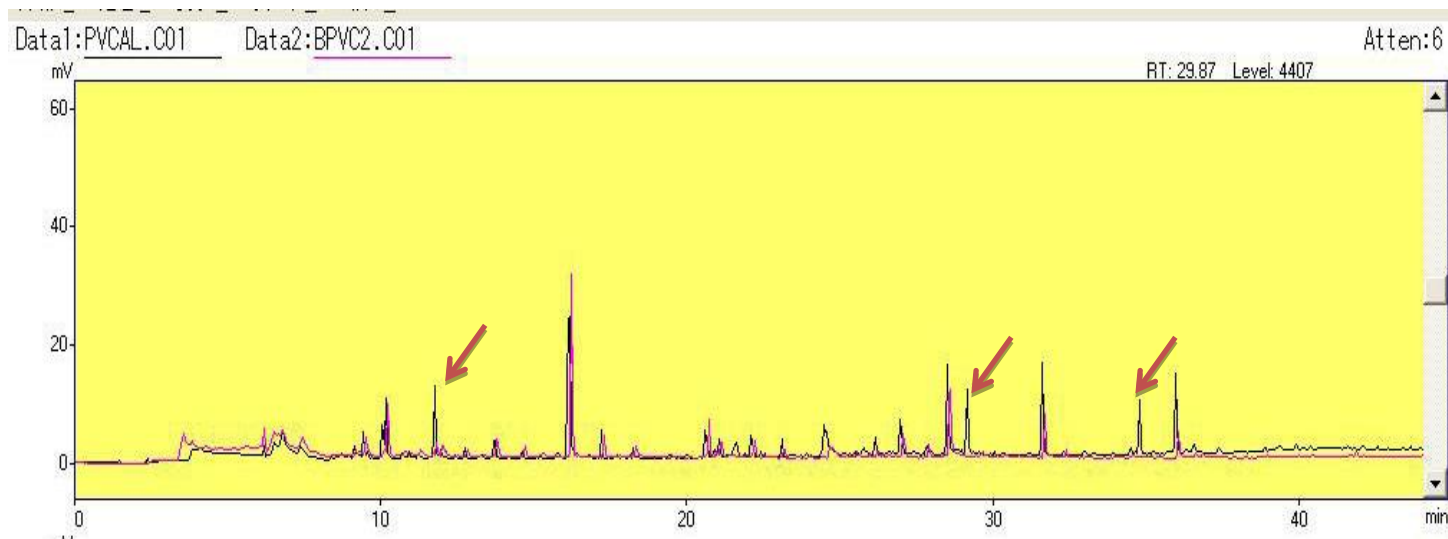
There are no new peaks and all the peak areas are almost the same when sheet PVC+PP are compressed, compared with the compression of sheet PVC and sheet PP, respectively.

When ball PVC+PP are compressed there is a new peak of the retention time 9.473min for two samples. While 5 samples have been tested, and for these two samples, the toluene generated during the compression is much less than that generated during the compression of PVC.

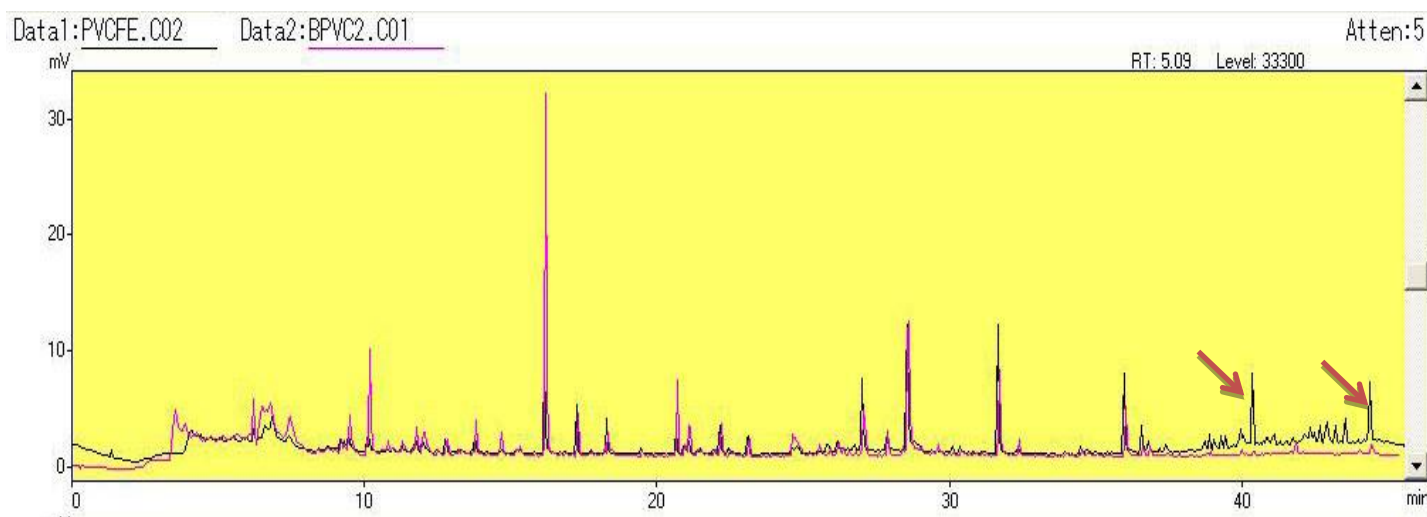
Since only in two samples, there is a new peak, it might be the error of GC-FID.

5.3.4 With metals

1)PVC+Al/ PVC+Fe



(a) PVC+Al



(b)PVC+Fe

Figure5.3.4-1Comparison of the chromatograms of VOCs generated during the compression of PVC+Al or Fe with the chromatograms of VOCs generated during the compression of PVC

Figure5.3.4-1 obviously shows that there are three new peaks when PVC+Al are compressed together, compared with the chromatogram of the VOCs generated during the compression of PVC. And there are two new peaks when PVC+Fe are compressed together.

Same samples have been tested on GC-MS. Table5.3.4-1 and Table5.3.4-2 compare the VOCs generated during the compression of PVC+Al and PVC+Fe with that of PVC.

**Table5.3.4-1 comparison of the VOCs generated during the compression of PVC+Alwith
that of PVC**

PVC+Al	PVC
2-butanone/2-pentanone	formaldehyde
Oxirane, 2,3-dimethyl-	sulfur dioxide
Methanol/ acetate(ester)/sulfurous acid/ methyl ester	carbonyl sulfide
Acetic acid	methyl alcohol
Butanal	2-methyl-1-propene
1,4-butanediol	(Z)-2-butene
Cyclohexan-1,4,5-trilo-3-one-1-carboxylic acid/1,4-oxathiane	ethyl alcohol
N-ethyl-N'-nitroguanidine/ formic acid, ethenyl ester	methyl isocyanide
propane	acetone
Pentanal	isopropyl alcohol
cyclobutanol	formic acid
tetrahydro-4H-pyran-4-ol	1,3-dichloro-2-propanol
Propane,2-(ethenyloxy)-	carbon disulfide
Butane,2,3-epoxy-	acetic acid
Cyclopropylcarbinol	butanal

1,2,4-trioxolane, 3,5-dipropyl,	2-butanone
Glycidol	ethyl acetate
Ethanol,2-nitro-	hexane
3-nitropropanoic acid	tetrahydro-furan
2-heptynoic acid	1-butanol
Toluene	benzene
Hexanal	formic acid, butyl ester
Propanamide,2-methyl-	toluene
2-acetylamino-3-hydroxy-propionic acid	hexanal
2-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-4-pyrazolyl)-5-nitrobenzoic acid	2,4-dimethyl-heptane
Silane,ethoxytriethyl-	N,N-dimethyl-acetamide
2-propenamide	hexane, 2,3,4-trimethyl- + ethylbenzene
Ethylbenzene	p-xylene
p-xylene	heptanal
Heptanal,octanal	cyclohexanone
Cyclohexanone	styrene
Ethanone	o-xylene
2-hexen-1-ol	phenol
Hexanoicacid	2,5-dimethyl-heptane
Nonane,octane	octanal
Cyclohexane	decane
2(5H)-Furanone, 3-methyl-	1,2,4-trimethyl-benzene
5-hepten-2-one,6-methyl-	2-ethyl-1-hexanol
Octanal	2,5,5-trimethyl-heptane
Oxetane,2-methyl-4-propyl-	5-ethyl-2-methyl-octane
2-propanol,1,1'-oxybis,	2-methyl-undecane
1-docanol	nonanal
1-pentanol,2-ethyl-4-methyl	undecane
Nonanal	6-ethyl-2-methyl-octane
	isothiocyanato-cyclohexane

**Table5.3.4-2 comparison of the VOCs generated during the compression of PVC+Fe with
that of PVC**

PVC+Fe	PVC
2-propanone,1-fluoro-	formaldehyde
Butanenitrile,2,3-dioxo-,dioxime	sulfur dioxide
Cyclobutylamine	carbonyl sulfide
Oriane,2,3-methyl-	methyl alcohol
Propane	2-methyl-1-propene
2-butanone	(Z)-2-butene
Butane,2-methyl-3-(methylthio)-	ethyl alcohol
Acetic acid	methyl isocyanide
Cyclohexan-1,4,5-trilo-3-one-1-carboxylic acid	acetone
Butanal,3-methyl-	isopropyl alcohol
pentanal	formic acid
1-Aziridineethanol	1,3-dichloro-2-propanol
2-hexynoic acid	carbon disulfide
Toluene	acetic acid
Hexanal	butanal
Hexane,2,4-dimethyl-	2-butanone
Silane,ethoxytriethyl-	ethyl acetate
2-propenamide,N-(1-cyclohexylethyl)-	hexane
Carbonic acid	tetrahydro-furan
1-hexanol	1-butanol
2-(4,5-dihydro-3-methyl-5-oxo-1-phenyl-4-pyrazolyl)-5-nitrobenzoic acid	benzene
Propanedioicacid,propyl-	formic acid, butyl ester
Heptanal	toluene
Nonane,decane	hexanal
1H-pyrrole,2,5-dihydro-1-nitroso-	2,4-dimethyl-heptane
5-hepten-2-one,6-methyl-	N,N-dimethyl-acetamide
Octane, 1-(ethenylthio)-	hexane, 2,3,4-trimethyl- +

	ethylbenzene
2-pentenal,2-methyl-/2(5H)-Furanone, 3-methyl-	p-xylene
Cyclohexane,isothiocyanato-	heptanal
n-Decanoic acid	cyclohexanone
Heptane,5-ethyl-2,2,3-trimethyl-	styrene
octanol	o-xylene
2-propanol,1,1'-oxybis-	phenol
1-hexanol,2-ethyl-	2,5-dimethyl-heptane
3-heptanol,5-methyl-	octanal
	decane
	1,2,4-trimethyl-benzene
	2-ethyl-1-hexanol
	2,5,5-trimethyl-heptane
	5-ethyl-2-methyl-octane
	2-methyl-undecane
	nonanal
	undecane
	6-ethyl-2-methyl-octane
	isothiocyanato-cyclohexane

According to Table5.3.4-1 and Table5.3.4-2 , most of the VOCs generated during the compression of PVC+Al and PVC+Fe are different from those generated during the compression of PVC. When PVC and metals are compressed together, some new VOCs are generated.

And types ofVOCs generated during the compression of PVC+Fe are less than those generated during the compression of PVC+Al. One reason is that Al has a higher chemical reactivity than Fe thus it might trigger more radicals during the compression.

After the compression, we found that PVC balls have static electricity. A hypothesis might be as follows----

As C-Cl bond is polar, the electron pair in the C-Cl bond will be dragged towards the Cl end, leaving the Cl slightly negative (δ^-) and the C slightly positive (δ^+). A quantity frequently used to describe this polar nature is the electronegativity. For element H, the electronegativity is 2.2, while for Cl, the electronegativity is 3.16. The bond dissociation energies(BDEs)which represent the strengths of chemical bonds is increasing with the increasing in electronegativity between the carbon and chlorine.[19] And via pseudo-first-order Stark effect, the orientation of a polar molecule can be enhanced by the combined action of static field.[20]

While during the compression of PVC with metals, when PVC has some static electricity, metals can eliminate the static electricity to a certain extent. When static electricity is eliminated, the polarity of the molecule decreases which means the electronegativity decreases as well as the bond dissociation energies. Finally the strength of C-Cl decreases, then it becomes more reactive. Since Al has a higher electric conductivity, thus it is more effective than Fe.

It is interesting to note that silane is detected during the compression of PVC with metals.

However, because of the time and resource constraint, it is difficult to determine what kind of chemicals the new peaks corresponds to in the GC-FID chromatograms.

5.4 Others

Two more interesting things are found during the experiment.

One is that there will be more VOCs generated during the compression with a much longer time; the other one is that after a certain number of compressions, there are nearly no VOCs generated. Sheet plastics are usually for over 5 times, while ball plastics can be over 20 times. Therefore, though sheet plastics can emit more things during each compression than ball plastics when they are of the same weight, as a whole, these two may emit about the same amount of VOCs.

These two phenomena can be explained by the viscoelastic creep of polymers. When a plastics material is under a constant stress, it will experience a time-dependent increase in strain until the material ultimately fails which have been discussed earlier in chapter3.4.

6. Conclusions and outlook

6.1 conclusions

1. It is the compression of plastics that generates some VOCs on account of the mechanical actions (pressure and friction), since most of the VOCs generated during compressions are different from those generated by the thermal degradation.
2. Even for the same kind of plastics, when they are compressed with different contact area, there will be different types and amount of VOCs generated, for the reason that the same kind of plastics with different shapes (ball or sheet) which has different contact area can produce different types and amounts of VOCs.
3. For a short time of compression, plastics with a larger contact area will generate more VOCs, on the fact that during the compression, sheet plastics which have a large contact area can generate more VOCs.
4. For the same kind of plastics, when compressed for a longer time at a time, they will generate more VOCs.
4. When plastics are compressed for a certain number of times, there will be nearly no new VOCs generated.
5. When PVC and PE or PVC and PP are compressed together, there is no synergy effect, because when they are compressed together, there is no change with the peak or the peak area.
6. When PVC and Al or PVC and Fe are compressed together, there are some new VOCs generated. PVC does react with Al or Fe during the compression.

6.2 Outlook

According to the conclusions, there is no need to separate different kinds of plastics when they are compressed. But it is better to compress plastics without metals.

Nowadays, plastics have a huge production and diversion in our society and the environment. More than one-third of the production volume of plastics is for disposable items. Many plastic products have a extremely short useful life span, measured in timescales of hours, minutes or even seconds. However, most of them are known to be persistent and pollute for years, decades or even centuries. The use of toxic chemicals in production and the potential emissions of toxic chemicals of the plastics waste will be hazardous to the human and the environment. Therefore a smarter use and safer way to process the waste is important, thus to understand various mechanisms is in urgent need.

The mechanisms used in this thesis to explain the reaction during the compression are just hypotheses. Further studies on the mechanisms still have to be done.

However, the best way is to reduce the use of plastic production. Something everyone can do, for example, using a recyclable bag instead of a regular bag when we go to the supermarket.

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