

AUTHOR

Kira Yang
PerkinElmer, Inc.
Shanghai, China

Yong Xu
PerkinElmer, Inc.
China - Eastern Region

Analysis of Rubber Samples by Pyrolysis Gas Chromatography-Mass Spectrometry

Introduction

As an important polymer material, rubber has been widely used in industrial and agricultural production and plays an irreplaceable role in thousands of everyday products. The study of the pyrolysis

behavior of rubber at high temperature is of great significance to the recovery and utilization of rubber, as well as the improvement of processing efficiency and the study of pyrolysis mechanism.

Since the 1980s, the combination of thermal pyrolysis and gas chromatography-mass spectrometry (GCMS) has created a new method of polymer characterization. It can effectively separate and identify the mixtures produced by thermal pyrolysis of polymers which provides a new way to study the thermal decomposition of polymers at the molecular level. The pyrolysis- gas chromatography-mass spectrometry (Py-GCMS) method is suitable for samples in any states and the samples need not to be separated and purified in advance. This feature is extremely beneficial for the study of insoluble and infusible polymers. It is an important aspect of pyrolysis research by inferring the structure of various chain segments and cross-linked bonds of the polymer compounds through pyrolysis products under different conditions to study the relationship between their structural properties.

In this study, the pyrolytic products of three rubber samples including trans-1,4-polyisoprene rubber, butadiene rubber and silicone rubber were analyzed by pyrolytic gas chromatography-mass spectrometry and the pyrolytic mechanism was also discussed.

Experiment Outline

Sample Preparation and Extraction

All rubber samples were obtained from customer laboratories and were cut into small pieces (ID 0.5 mm) using a cutter. Then the sample was put into a quartz tube by a tweezer before analysis. Nitrile rubber gloves were used to avoid contamination during the whole sample preparation process.

Instrumentation

The PerkinElmer Clarus® SQ8 GC/MS operating in electron ionization (EI) mode with CDS Model 6150 Pyroprobe was used to perform these experiments. The 6150 pyroprobe was connected to GC with a heated sample line. The conditions are presented in Table 1. Each sample was heated to 150, 200, 300, 400, 500, 600, 700 and 800 °C for 15 s, respectively. A PerkinElmer Elite 5MS column (30 m x 0.25 mm x 0.25 µm) was used to separate the pyrolysis products.

Table 1. Analytical parameters.

CDS 6150 Pyroprobe Parameters	
Set-Point	150, 200, 300, 400, 500, 600, 700 and 800 °C for 15 s
Interface	300 °C
Valve Oven	300 °C
Transfer Line	325 °C
GC Parameters	
Analytical Column	Elite-5MS (30 m x 0.25 mm x 0.25 µm)
Inlet Temp	280 °C
Carrier Gas Flow Rate	1 mL/min
Split Ratio	20:1
Initial Oven Temp	35 °C
Oven Hold	2.0 min
Ramp	20 °C/min
2 nd Oven Temp	280 °C
Oven Hold	4 min
MS Parameters	
Mass Range (amu)	33 to 550
GC Inlet Line Temp	280 °C
Ion Source Temp	250 °C
Function Type	SIFI
Ionization	EI

Results and Discussion

The mechanism of polymer thermal pyrolysis depends on the type of polymer. The characteristics and relative yield of the products are also related to the design of the pyrolyzer and experimental conditions.

Polyisoprene Used in Golf Shells

Polyisoprene (PI) is a polymer of isoprene (2-Methyl-1,3-butadiene). Trans-polyisoprene (TPI) is one of isomers of PI, which is used for making golf shells. The chemistry structural formula of TPI is shown in Figure 1. Figure 2 shows the total

ion chromatograms (TIC) for a series of runs on TPI samples, heating sequentially to 150, 200, 300, 400, 500, 600, 700 and then 800 °C. The list of pyrolytic products is shown in Table 2. At 150 °C, the pyrolytic products include 2,2-Dimethyl-4-octenal (RT=9.61 min) and Diethyl Phthalate (RT=10.34 min). 2,2-Dimethyl-4-octenal is the product of rearrangement oxidation of isoprene dimer. Diethyl Phthalate (DEP) is a commonly used plasticizer. At 200 °C, Hexanoic anhydride (RT=10.61 min) was obtained besides the two pyrolytic products mentioned above. At 300 °C, more pyrolytic products were obtained. The main products were still 2,2-Dimethyl-4-octenal and Hexanoic anhydride. At 400 °C, the pyrolytic product was mainly D-Limonene (RT=6.42 min). It is a dimer of isoprene which is a food additive with high economic value. At 500 °C, the main pyrolytic product was still D-Limonene. The other products included Isoprene (RT=1.89 min), 4-Methyl-1-(1-methylethenyl)-cyclohexene (RT=6.22 min). Isoprene is the Polyisoprene monomer and 4-Methyl-1-(1-methylethenyl)-cyclohexene is an isomer of isoprene dimer. The peak of Isoprene was relatively flat and the peak area was small. It indicated that the yield of Isoprene was low at this temperature, and Isoprene wasn't produced at the moment of pyrolysis. Isoprene should be produced by the secondary reaction of isoprene multimer in the pyrolyzer. At 600 °C, the retention time of the peak for Isoprene moved forward to 1.81 min, and the peak became sharper. A peak of p-Xylene was observed on the chromatogram (RT=4.89 min). When the pyrolysis temperature increased to 700 °C and 800 °C, the main products of pyrolysis were Isoprene and D-Limonene and the area percentage of Isoprene went up, indicating more complete pyrolysis. The amount of small molecule products also increased with the increase of pyrolysis temperature, including carbon dioxide (RT=1.53 min), Propylene (RT=1.57), Toluene (RT= 3.78 min), o-Methylphenol (RT=6.71 min), 1, 2-Dihydronaphthalene (RT=7.45 min) and so on. Figure 3 shows the relationship between the area percentages of three main pyrolysis products of polyisoprene and the pyrolysis temperature. When the pyrolysis temperature was lower than 300 °C, the yield of 2,2-Dimethyl-4-octenal increased with the increase of pyrolysis temperature. At that time, the yield of Isoprene dimer was very low and monomer wasn't produced. When the pyrolysis temperature increased from 300 to 400 °C, the yield of D-Limonene soared to 57.32% to become the main product. While the yield of 2,2-Dimethyl-4-octenal decreased from 10.77% to 1.11%. When the pyrolysis temperature was set to 500 °C, the yield of Isoprene monomer was significantly increased to 25.32%, and the yield of D-Limonene gradually decreased. The yield of Isoprene stabilized from 500 to 800 °C of pyrolysis temperature. The yield of D-Limonene gradually decreased and large number of small molecule compounds were produced in this temperature range (Table 2). The pyrolytic mechanism of trans-polyisoprene is as shown in Figure 4.

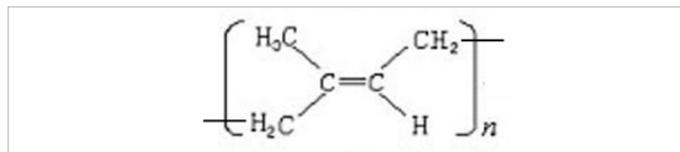


Figure 1. Chemistry structural formula of TPI.

Table 2. Pyrolytic product names of TPI at 150, 200, 300, 400, 500, 600, 700 and 800 °C of pyrolysis temperature. (The green cell represents that the product was observed at the pyrolysis temperature.)

RT	CAS	Compound Name	150 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
1.52	124-38-9	Carbon dioxide								
1.57	115-07-1	Propene								
1.62	107-01-7	2-Butene								
1.80	78-79-5	Isoprene								
2.07	591-93-5	1,4-Pentadiene								
2.22	691-38-3	cis-4-Methyl-2-Pentene								
2.31	534-22-5	2-Methylfuran								
2.48	96-38-8	5-Methylcyclopentadiene								
2.52	628-41-1	1,4-Cyclohexadiene								
2.58	2235-12-3	1,3,5-Hexatriene								
3.47	4054-38-0	1,3-Cycloheptadiene								
3.75	4313-57-9	2,5-Dihydrotoluene								
3.77	108-88-3	Toluene								
3.80	4313-57-9	2,5-Dihydrotoluene								
4.86	78-93-3	2-Butanone								
4.89	106-42-3	p-Xylene								
5.57	NIST 369964*	2-Ethylbutyric acid, 2-formylphenyl ester								
5.75	138-86-3	Limonene								
6.11	95-63-6	1,2,4-Trimethylbenzene								
6.17	NIST 326005*	1-Hexanol, 2-(hydroxymethyl)-								
6.22	586-67-4	1-Isopropenyl-4-methyl-1-cyclohexene								
6.36	460-01-5	2,6-Dimethyl-1,3,5,7-octatetraene, E,E-								
6.40	5989-27-5	D-Limonene								
6.58	NIST 112559*	2,5-Dimethyl-2-(2-tetrahydrofuryl)tetrahydrofuran								
6.71	108-39-4	m-Methylphenol								
6.74	53398-86-0	trans-2-Hexenyl caproate								
6.94	1195-32-0	p-Isopropenyl toluene								
7.12	18368-95-1	1,3,8-p-Menthatriene								
7.15	NIST 405690*	Fumaric acid, 2-methylphenyl dodec-2-en-1-yl ester								
7.26	5811-48-3	Bicyclo[2.2.1]heptan-2-one, 1,3,7,7-tetramethyl-								
7.40	6508-22-1	2-Oxatricyclo[3.3.1.1(3,7)]decane, 1-methyl-								
7.45	447-53-0	Naphthalene, 1,2-dihydro-								
7.75	833-85-2	Benzenepentanoic acid, 4-methyl-6-oxo-								
8.40	30390-60-4	2,2-Dimethyl-4-octenal								
8.81	62338-54-9	1,5-Cycloundecadiene, 8,8-dimethyl-9-methylene-								
8.90	4884-24-6	[1,1'-Bicyclopentyl]-2-one								
9.10	74421-03-7	2-Decene, 2,4-dimethyl-								
9.36	30390-60-4	2,2-Dimethyl-4-octenal								
9.43	NIST 299360*	Hexanoic acid, tridec-2-ynyl ester								
9.61	30390-60-4	2,2-Dimethyl-4-octenal								
10.06	2051-49-2	n-Hexanoic acid anhydride								
10.34	84-66-2	Diethylphthalate								

* The compound has no CAS number in NIST library. Here NIST registry number is used to identify compounds.

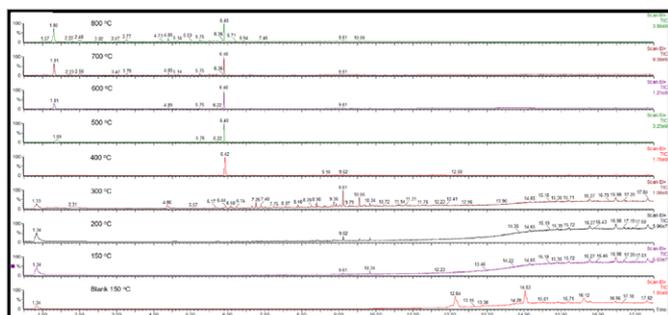


Figure 2. Total ion chromatograms (TIC) for a series of runs on TPI samples and blank run. (The samples were heated sequentially to 150°, 200°, 300°, 400°, 500°, 600°, 700° and then 800°C. The heating temperature for blank run was 150°C.)

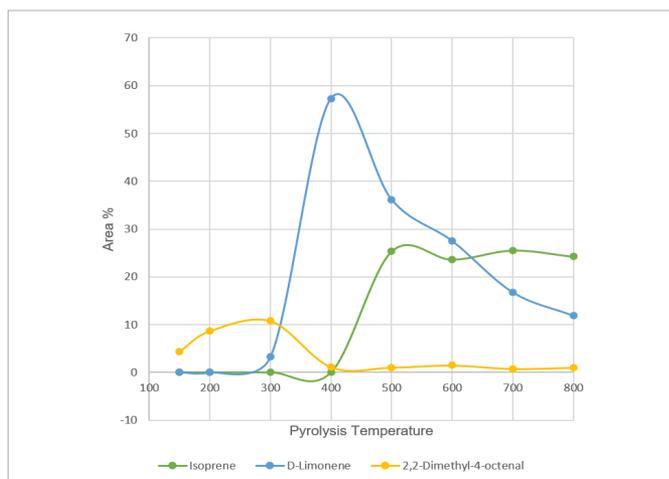


Figure 3. The relationship between the area percentages of three main pyrolysis products of Polyisoprene and the pyrolysis temperature.

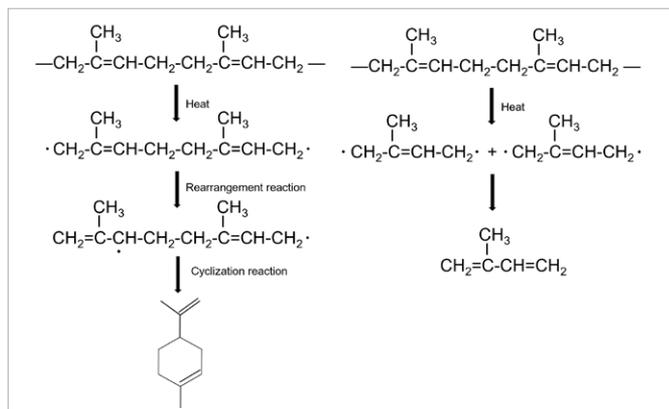


Figure 4. The pyrolytic mechanism of TPI.

Butadiene Rubber for Tires

Butadiene rubber (BR) is a synthetic rubber polymerized by 1,3-Butadiene. The cis content of BR, named Cis-polybutadiene, is more than 95%. Cis-polybutadiene is particularly suitable for the manufacture of automobile tires and cold-resistant products. The chemistry structural formula is shown in Figure 5. Figure 6 shows the total ion chromatograms (TIC) for a series of runs on Cis-polybutadiene samples, heating sequentially to 150, 200, 300, 400, 500, 600, 700 and then 800 °C. The list of pyrolytic

products is shown in Table 3. At 150 and 200 °C of pyrolysis temperature, there are three pyrolytic products, including Acetophenone (RT=6.81 min), Decanal (RT=7.78 min) and Diethyl Phthalate (DEP) (RT=10.34 min). Decanal and Acetophenone may be additives in the production of butadiene rubber. At 400 °C, the variety of pyrolytic products increased, including 4-Ethenylcyclohexene (RT=4.63 min), 1,2,4-Trivinylcyclohexane (RT=7.66 min), trans -5,6-Divinyl-1-cyclooctene (RT=7.47 min), cis-5,6-Divinyl-1-cyclooctene (RT=8.21 min) and Pyrene (RT=13.27 min). 4-Ethenylcyclohexene is a dimer of butadiene. 1,2,4-Trivinylcyclohexane, trans -5,6-Divinyl-1-cyclooctene and cis-5,6-Divinyl-1-cyclooctene are the trimer. Pyrene is a tetramer. At this pyrolysis temperature, 1,2-Dihydro-2,2,4-trimethylquinoline (RT=9.50 min) was also one of the main pyrolytic products. The peak profile of 4-Ethenylcyclohexene was broad and gentle which indicated the product wasn't produced by primary reaction pyrolysis. It should be produced by the secondary reaction in the pyrolyzer. When the pyrolysis temperature was set to 500 °C, 1,3-Butadiene was produced (RT=1.73 min). At this temperature, the peak of 4-Ethenylcyclohexene became sharper and the retention time moved forward (RT=4.53 min). Many small molecule compounds was also produced at this temperature, such as 1,4-Pentadiene (RT=2.03 min), 1,3-Cyclohexadiene (RT=2.83 min), Toluene (RT=3.88 min), 4-Ethylcyclohexene (RT= 4.71 min), p-Xylene (RT=5.16 min) and o-Methylstyrene (RT=6.51 min). In Figure 6, the retention time for most products was in the range of 6.81-14 min when the pyrolytic temperature was 400 °C. However, the retention time for the products significantly moved forward, from 1.50 to 12.16 min, at 500 °C of pyrolysis temperature. The explanation is that the extent of pyrolysis increased at 500 °C and the pyrolytic products were turned from compounds with large molecular weight to compounds with small molecular weight. At 600 °C, the peak of 1,3-Butadiene (RT=1.67 min) became sharp, indicating that Cis-polybutadiene was instantaneously cracked to produce 1,3-Butadiene at this temperature. The area percentage of 1,3-Butadiene (22.48%) was higher than that of 4-Ethenylcyclohexene (16.29%) which means that 1,3-Butadiene became the main product. In addition, a variety of products with small molecule weight were observed on TIC with the retention time from 1.70 to 4.70 min (Table 3), indicating that the extent of pyrolysis further increased. At this temperature, the pyrolytic products which retention time was later than 4.50 min were similar to those produced at 500 °C of pyrolysis temperature. At 700 and 800 °C, the types of pyrolytic products were similar to those at 600 °C. But the area percentage of 1,3-Butadiene and 4-Ethenylcyclohexene was lower than that at 600 °C, indicating that the yield of other pyrolytic products increased. Figure 7 shows the relationship between the area percentage of 1,3-butadiene and 4-Ethenylcyclohexene and the pyrolysis temperature. When the pyrolysis temperature was lower than 300 °C, the two compounds weren't produced. At 400 °C of pyrolysis temperature, the yield of 4-Ethenylcyclohexene increased to 32.74% to become the main product. At 500 °C, the yield of 1,3-Butadiene increased to

17.36%, and the yield of 4-Ethenylcyclohexene decreased to 20.21%. 4-Ethenylcyclohexene was still the main product. After the pyrolysis temperature was set to 600 °C, 1,3-Butadiene became the main product with 22.48% of yield. The yield of 4-Ethenylcyclohexene gradually decreased. At 700 °C, the yield of 1,3-Butadiene and 4-Ethenylcyclohexene all decreased,

and the yield of other pyrolytic products increased. When the pyrolysis temperature was 800 °C, the yield of 1,3-Butadiene and 4-Ethenylcyclohexene was slightly lower than that at 700 °C, reflecting the larger amount of other products was produced. The pyrolysis mechanism of Cis-polybutadiene is shown in Figure 8.

Table 3. Pyrolytic product names of Cis-polybutadiene at 150, 200, 300, 400, 500, 600, 700 and 800 °C of pyrolysis temperature. (The green cell represents that the product was observed at the pyrolysis temperature.)

RT	CAS	Compound Name	150 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
1.52	124-38-9	Carbon dioxide								
1.57	115-07-1	Propene								
1.58	7446-09-5	Sulfur dioxide								
1.62-1.73	106-99-0	1,3-Butadiene								
1.80	563-45-1	3-Methyl-1-butene								
1.86	591-93-5	1,4-Pentadiene								
1.90	542-92-7	1,3-Cyclopentadiene								
1.96	142-29-0	Cyclopentene								
2.49	592-57-4	1,3-Cyclohexadiene								
2.68	71-43-2	Benzene								
2.74	14548-32-4	4-Methylenecyclopentene								
2.83	110-83-8	Cyclohexene								
2.96	7736-34-7	(5Z)-1,5-Heptadiene								
3.05	1541-23-7	1,5-Heptadiene								
3.56	22038-69-3	(E,E)-1,3,6-Octatriene								
3.59	50592-72-8	(5E)-3-Methyl-1,5-heptadiene								
3.77	108-88-3	Toluene								
4.21	4894-62-6	3-Methyl-1,5-heptadiene								
4.29	4974-27-0	2,6-Octadiene								
4.40	4974-27-0	2,6-Octadiene								
4.46	4190-06-1	1,5-Dimethyl-1,4-cyclohexadiene								
4.49	100-40-3	4-Ethenylcyclohexene								
4.58	925-52-0	5-Methyl-1,3,6-heptatriene								
4.67	3742-42-5	4-Ethylcyclohexene								
4.74	930-99-4	cis-Bicyclo[3.3.0]-2-octene								
4.80	100-41-4	Ethylbenzene								
4.84	4982-20-1	1,4-Dimethylenecyclohexane								
4.89	4190-06-1	1,5-Dimethyl-1,4-cyclohexadiene								
5.14	106-42-3	p-Xylene								
5.23	108-38-3	m-Xylene								
5.26	95-47-6	o-Xylene								
5.51	37689-19-3	1-(2-Propenyl)cyclopentene								
5.55	5664-10-8	Allylidene-cyclohexane								
5.73	103-65-1	Propylbenzene								
5.97	611-14-3	o-Ethyltoluene								
6.27	NIST 305392*	Tricyclo[7.1.0.0[1,3]]decane-2-carbaldehyde								
6.50	611-15-4	o-Methylstyrene								
6.60	766-82-5	3-Methylphenylacetylene								
6.81	98-86-2	Acetophenone								
7.10	68284-23-1	4,7-Methano-1H-indene, octahydro-2-methylene-								

Table 3. continued..

RT	CAS	Compound Name	150 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
7.43	NIST 151062*	5,6-Dimethylene-1-cyclooctene								
7.45	53264-71-4	trans-5,6-Divinyl-1-cyclooctene								
7.65	2855-27-8	1,2,4-Trivinylcyclohexane								
7.78	112-31-2	Decanal								
8.20	53264-72-5	cis-5,6-Divinyl-1-cyclooctene								
9.50	147-47-7	1,2-Dihydro-2,2,4-trimethylquinoline								
9.53	112-52-7	n-Dodecyl chloride								
9.60	40135-99-7	4-Methylilolidine								
10.16	71673-32-0	1,11-Hexadecadiyne								
10.24	51487-38-8	1,5,9,13-Tetradecatetraene								
10.33	84-66-2	Diethyl Phthalate								
10.50	74708-73-9	1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-								
12.03	82304-66-3	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione								
12.16	NIST 336384*	Methyl 3-cis,9-cis,12-cis-octadecatrienoate								
12.26	51487-38-8	1,5,9,13-Tetradecatetraene								
13.27	129-00-0	Pyrene								
13.49	NIST 187029*	(7a-Isopropenyl-4,5-dimethyloctahydroinden-4-yl) methanol								

* The compound has no CAS number in NIST library. Here NIST registry number is used to identify compounds.

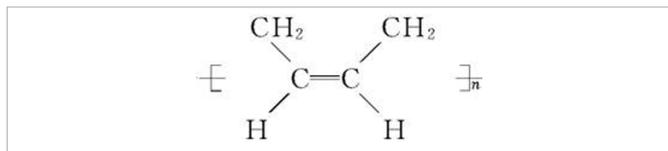


Figure 5. Chemistry structural formula of Cis-polybutadiene.

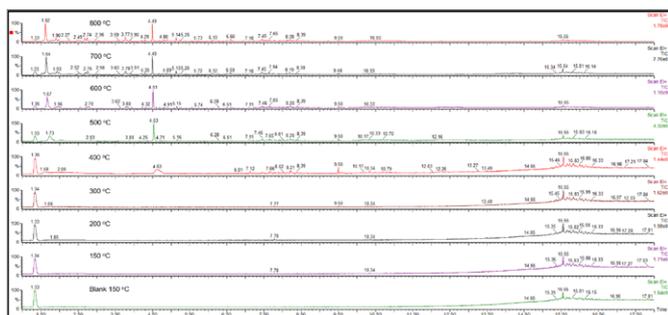


Figure 6. Total ion chromatograms (TIC) for a series of runs on Cis-polybutadiene samples and blank run. (The samples were heated sequentially to 150°, 200°, 300°, 400°, 500°, 600°, 700° and then 800°C. The heating temperature for blank run was 150°C.)

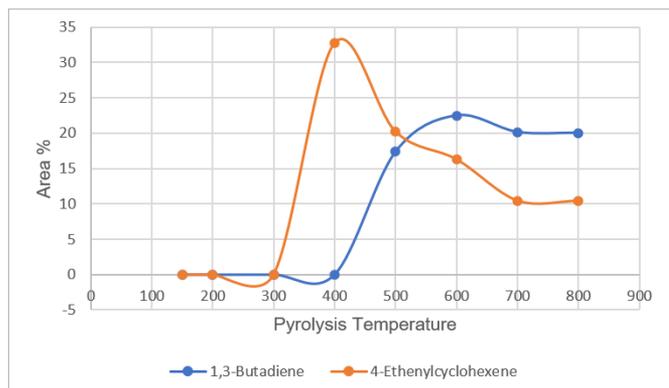


Figure 7. The relationship between the area percentages of two main pyrolysis products of Cis-polybutadiene and the pyrolysis temperature.

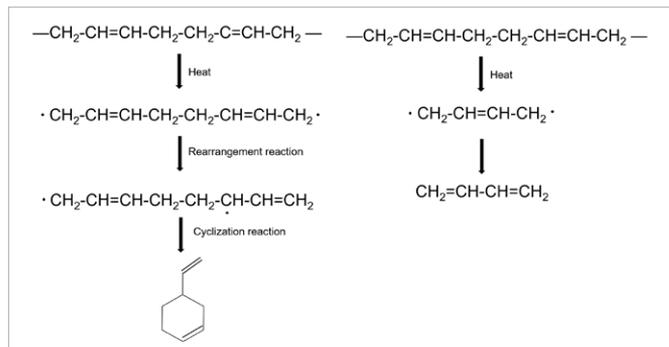


Figure 8. The pyrolytic mechanism of Cis-polybutadiene.

Silicone Rubber in Medical Usage

Silicone rubber refers to a rubber which main chain consists of alternating silicon and oxygen atoms, and two organic groups are usually attached to the silicon atoms. It is widely used in the medical industry. General silicone rubber is mainly composed of siloxane chain links containing methyl groups and a small amount of vinyl groups. If phenyl is introduced, the high and low temperature resistance of silicone rubber can be improved, and the introduction of trifluoropropyl and cyano groups can improve the temperature and oil resistance of silicone rubber. Figure 9 shows a chemistry structural formula of silicone rubber. R, R' and R'' are methyl, phenyl, vinyl or trifluoropropyl. In order to better understand the thermal behavior, a silicone rubber sample was treated to multiple temperatures. Figure 10 shows the total ion chromatograms (TIC) for a series of runs on the same sample, heating sequentially to 150, 200, 300, 400, 500, 600, 700 and then 800 °C. The list of pyrolytic products is shown in Table 4. There are two peaks on the TIC at 150 °C of pyrolysis temperature. The retention time (RT) is 11.68 min for a cyclic compound containing three oxygen atoms and six silicon atoms and 12.29 min for 1,2-Diphenyltetramethyldisilane. They are compounds similar to dimers and trimers of siloxanes. With the increase of the pyrolysis temperature, from 150 to 500 °C, the two peaks became higher and higher. At 200 °C, plasticizer peaks appeared on the TIC, with 11.77 min of retention time for Di-iso-Butyl phthalate (DIBP) and 12.24 min for Dibutyl phthalate (DBP). As polymer additives, they were released from silicone rubber at a low pyrolysis temperature. There were peaks for Acetophenone (RT=6.82 min), Phthalic anhydride (RT=8.74 min), Diphenyl ether (RT=9.27min) and Bis[di(trimethylsiloxy)phenylsiloxy]trimethylsiloxyphenylsiloxy (RT=12.97 min) on the TIC at 300 °C of pyrolysis temperature. Acetophenone is the main decomposition product of Dicumyl peroxide (DCP). DCP is the main vulcanizing agent for vulcanized silicone rubber. Phthalic anhydride should be derived from the thermal decomposition reaction of the plasticizer. The appearance of Diphenyl ether and Bis[di(trimethylsiloxy)phenylsiloxy]trimethylsiloxyphenylsiloxy illustrated that not only the primary pyrolysis reaction but also the secondary reaction of pyrolysis occurred, which made the products complicated. When the pyrolysis temperature increased to 400 °C, the peaks for carbon dioxide (RT=1.58 min), 1,3-Diphenyltetramethyldisiloxane (RT=10.81 min) and Di(ethylhexyl) phthalate (RT=14.63 min) were observed on the TIC. 1,3-Diphenyltetramethyldisiloxane is a typical dimer of siloxane. Di(ethylhexyl) phthalate is the most widely used plasticizer. At 500 °C, there were a series of peaks from

5.0 to 8.5 min on the TIC. The main pyrolytic product were still DBP (RT=12.23 min), 6,8-Difluoro-2,2,4,4,6,6,7,7,8,9,9-decamethyl-[1,3,5,2,4,6,7,8,9]trioxahexasiloxane (RT= 11.68min), 1,2-Diphenyltetramethyldisilane (RT=12.29 min) and Diphenyl ether (RT=9.27 min), indicating the scission incompletely of silicon-oxygen chain at this temperature. In addition to the primary pyrolysis reaction, a large number of secondary pyrolysis reactions and secondary random scission reactions occurred, resulting in complex products. At 600 °C of pyrolysis temperature, the main peaks on the chromatogram were 1,3,5-Tri-tert-butylbenzene (RT=10.83 min) and Diphenyl ether (RT=9.27 min). At the same time, some new products were observed, including Hexamethylcyclotrisiloxane (RT=4.33 min), 9-Chloro-9-methyl-9-silafluorene (RT=7.79 min), 2-[[[(Trimethylsilyloxy)carbonyl]phenyl]2-[(trimethylsilyloxy)benzoate (RT=11.87 min) and 4-Trimethylsilyloxybenzoic anhydride (RT=12.74 min). When the pyrolysis temperature was set to 700 °C, the products with small molecular weight were observed, such as Difluorodimethylsilane (RT=1.69 min), Dimethylsilyl ether (RT=2.26 min), Benzene (RT=2.82 min), Toluene (RT= 3.86 min) and Hexamethylcyclotrisiloxane (RT=4.27 min). It shows that the silicone rubber degraded to siloxane dimers, and the functional groups on the siloxane branches also decomposed. The compounds eluted after five minutes were silicon-containing heterocyclic compounds. At 800 °C of pyrolysis temperature, a regular pattern distribution of peaks was observed on the TIC. The products included a series of hydrocarbon compounds from C3 to C 29, The partial enlarged view is shown in Figure 11. The corresponding compounds are shown in Table 5. They are the characteristic peaks, including diene, alkene and alkane, formed from long-chain alkanes random scission, indicating the carbon chain scission and recombination reactions at this temperature.

The products were quite different at different pyrolysis temperature for silicone rubber. The pyrolytic products include siloxane trimers, dimers and secondary reaction products as well as some additives when the temperature was lower than 600 °C. Small molecular compounds were observed at 700 °C, such as Difluorodimethylsilane. There were a series of peaks including diene, alkene and alkane on the TIC at 800 °C. Some products were observed repeatedly at different pyrolysis temperatures, such as 1,3-Diphenyltetramethyldisiloxane, Trioxahexasiloxane, 1,2-Diphenyltetramethyldisilane and Diphenyl ether. The pyrolysis process started at the silicon-oxygen chain scission to generate free radicals, which consequently to form various products.

Table 4. Pyrolytic product names of silicone rubber at 150, 200, 300, 400, 500, 600 and 700 °C of pyrolysis temperature. (The green cell represents that the product was observed at the pyrolysis temperature.)

RT	CAS	Compound Name	150 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
1.58	124-38-9	Carbon dioxide								
1.69	353-66-2	Difluorodimethylsilane								
2.26	3277-26-7	Dimethylsilyl ether								
2.82	71-43-2	Benzene								
3.86	108-88-3	Toluene								
4.27	541-05-9	Hexamethylcyclotrisiloxane								
4.33	541-05-9	Hexamethylcyclotrisiloxane								
5.16	100-42-5	Styrene								
5.69	2530-10-1	Dimethylthienylcetone								
5.91	556-67-2	2-(tert-Butyldimethylsilyloxy)benzylidene acetophenone								
6.11	108-95-2	Phenol								
6.13	100-47-0	Benzonitrile								
6.14	24599-58-4	2,5-Dimethoxytoluene								
6.73	95-48-7	o-Methylphenol								
6.82	98-86-2	Acetophenone								
7.21	13688-68-1	9,9-Dimethyl-9-silafluorene								
7.24	6807-17-6	4,4'-(1,3-Dimethylbutylidene)bisphenol								
7.36	NIST 282214*	1-Cyclohexyldimethylsilyloxy-3-phenylpropane								
7.79	18090-00-1	9-Chloro-9-methyl-9-silafluorene								
8.34	81834-51-7	Cyclopentene, 3-methyl-1-(trimethylsilyloxy)-								
8.48	69460-62-4	(4aS,8R)-4a,8-Dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one								
8.74	85-44-9	Phthalic anhydride								
8.83	NIST 462327*	2-Hydroxy-5-methylbenzophenone, trimethylsilyl ether								
9.27	101-84-8	Diphenyl ether								
10.05	132-64-9	(1S,4R,5S)-1-Methyl-4-(prop-1-en-2-yl)spiro[4.5]dec-7-ene-8-carbaldehyde								
10.46	86-73-7	Fluorene								
10.81	56-33-7	1,3-Diphenyltetramethyldisiloxane								
10.83	1460-02-2	1,3,5-Tri-tert-butylbenzene								
11.28	NIST 157270*	Norcaradiene, 2,3,4,5-tetramethyl-7,7-diphenyl-								
11.59	143586-27-0	4-tert-Butyl-2-phenylphenol								
11.68	NIST 311722*	6,8-Difluoro-2,2,4,4,6,7,7,8,9,9-decamethyl-[1,3,5,2,4,6,7,8,9]trioxahexasiloxane								
11.77	84-69-5	Di-iso-Butyl phthalate-DIBP-								
11.87	NIST 408129*	2-(((Trimethylsilyloxy)carbonyl)phenyl 2-((trimethylsilyloxy)benzoate								
12.24	84-74-2	Dibutyl phthalate (DBP)								
12.29	1145-98-8	1,2-Diphenyltetramethyldisilane								
12.43	NIST 461649*	3-Hydroxy-4-methoxybenzaldehyde (TBDMS)								
12.74	NIST 375021*	4-Trimethylsilyloxybenzoic anhydride								
12.97	NIST 306774*	Bis[di(trimethylsilyloxy)phenylsiloxy]trimethylsilyloxyphenylsiloxane								
13.27	789-24-2	9-Phenylfluorene								
14.22	NIST 153858*	Bicyclo[3.3.0]octan-2-one, [7-(1-trimethylsilyl-1-phenyl)methylene]								
14.63	117-81-7	Di(ethylhexyl) phthalate								

* The compound has no CAS number in NIST library. Here NIST registry number is used to identify compounds.

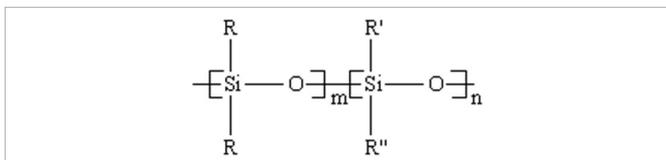


Figure 9. Chemistry structural formula of silicone rubber. R, R' and R'' are methyl, phenyl, vinyl and trifluoropropyl.

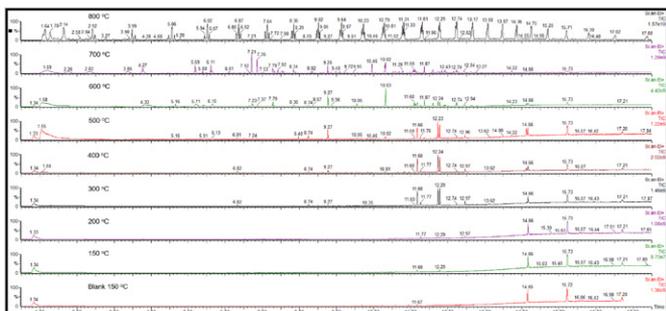


Figure 10. Total ion chromatograms (TIC) for a series of runs on the silicone rubber samples and blank run. (The samples were heated sequentially to 150°, 200°, 300°, 400°, 500°, 600°, 700° and then 800°C. The heating temperature for blank run was 150°C.)

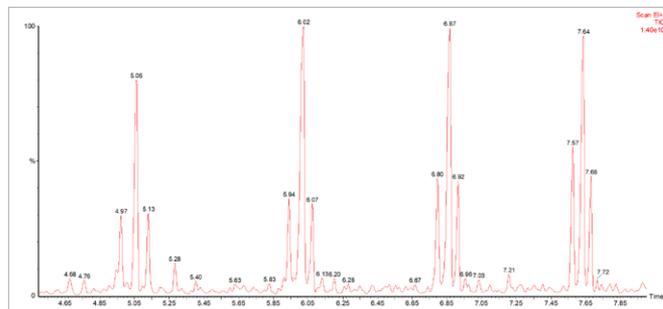


Figure 11. The partial enlarged view of TIC for the run on the Silicone rubber samples at 800°C.

Summary

The thermal degradation behavior of three rubber samples were studied by pyrolysis-gas chromatography-mass spectrometry. The pyrolysis and the analysis of products was easily performed using a PerkinElmer Clarus SQ8 GC/MS coupled with a CDS Model 6150 Pyroprobe.