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Study on Molecular Structure of High Purity Natural Rubber

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Abstract. Pyrolysis production and structure of molecule of high purity natural rubber (NR) were studied. Results show that there is no stretching vibration absorption peak of N-H group on 3280cm^{-1} and vibration compound peak of C-N group and N-H group in amide group on 1540cm^{-1} in high purity NR comparing to NR. Pyrolysis productions of high purity NR are less than that of NR. Main pyrolysis products of high purity NR are Limonene, 1, 3-Pentadiene and 4-ethenyl-1, 4-dimethyl-Cyclohexene, which is 58.98% of mass fraction of total pyrolysis productions.

Introduction

NR is a polymer made by coagulating and drying NR that is from Hevea brasiliensis, so it is a bio-synthetic natural high polymer material. As the need of growth physiological while Hevea brasiliensis are growing, a lot of substances are participators in the metabolic processes. According to analysis of Altman [1], besides rubber hydrocarbon and liquid, natural latex from Hevea brasiliensis contains nine types of non-rubber substances, including inorganic elements, protein, amino acids, sugars, organic acids, lipid, vitamin, nucleic acid and alkaloid. Non-rubber substances are closely relative to property of NR, so the relation between property and non-rubber substances has been widely studied. Gregg [2] et al. found in 1973 that non-rubber substances in white crepe have significant effect on property of rubber, particularly on scorch, heat building and tear strength. A.B.Othman [3] et al. discovered in 1996 that some amino acids can increase elastic modulus and reduce relaxation rate of vulcanizate. S.Tuampoemsab[4] et al. confirmed in 2007 the effect of protein and lipid on thermal aging behavior of purified NR. Kanjanee Nawamawat [5] et al. also confirmed in 2010 the significance effect of protein on property of NR during storage. Zhao qin-xiu[6] et al. in 1981 studied extraction and separation of phospholipid in NR latex and the effect of phospholipid on property of NR. M.Morimoto [7] found in 1985 that tocotrienols play an important role in anti-thermal aging of NR. The structure is closely relative to property of NR, however, the change of molecular structure after non-rubber substances in NR are removed has not been known. Composition and structure of polymer can be identified through the use of pyrolysis gas chromatography / mass spectrometry [8, 9, 10]. The pyrolytic products of NR are contributed to understanding of macromolecular structure of NR. In our work, high purity NR extracted most of non-rubber substances are analyzed by pyrolysis gas chromatography / mass spectrometry, and relationship between pyrolytic products and property of NR is studied.

Experiment

Materials

Fresh NR latex was provided by Tuanjie Farm in Guangdong province, P.R. of China. Formic acid and sodium lauryl sulphate were of chemical grade. Others were Industrial grade.

Preparation of NR sample

Preparation of High Purity NR

Sodium lauryl sulphate was added into fresh NR latex, and was stirred fully. The level of sodium lauryl sulphate was 1.0 % of weight of fresh NR latex and was made into sodium lauryl sulphate solution of 5-10% with clean water before added into fresh NR latex. Alkaline protease was added and was stirred fully. The level of alkaline protease was 0.1 % of weight of fresh NR latex and dissolve with water before added. After stand at room temperature for 24 hours, fresh NR latex containing sodium lauryl sulphate and alkaline protease was centrifuged by Type 410 centrifuge at rotate speed of 7000r/min. Then the concentrated NR latex was diluted to 25% with water and stand for 24 hours. The latex was dealt 3-4 times repeatedly according to above procedure to remove non-rubber substances such as protein, amino acids, lipid and so on. Finally the concentrated NR latex was diluted to 25% with water, and was coagulated with absolute ethyl alcohol that is 1-2 times weight of the latex. The coagulum was creped and granulated. The granule was soaked in clean water for 24 hours to remove water-soluble non-rubber substances. The granule was drained, then extracted with absolute ethyl alcohol for 24 hours to remove alcohol-soluble non-rubber substances. Finally the granule was dried in vacuum drying oven at 60^0C for 36 hours

Preparation of Control Sample

Fresh NR latex containing 0.04% ammonia was coagulated with formic acid. The level of formic acid was 0.4% of weight of dry rubber in fresh NR latex, and the formic acid was diluted to 5% before adding into fresh NR latex. (the other calculation should be make for the formic acid needed to neutralize the ammonia in fresh NR latex.) The coagulum was take out 18 hours after formic acid solution was put into fresh NR latex, then was creped, size-reduced and dried in an oven at 115 ^{0}C for 5 hours.

Test Method

Infrared spectrometry was carried by PERKIN ELMER Spectrum GX Type Fourier transform infrared spectrometer, and resolution was $4cm^{-1}$.

Pyrolysis of sample was carried out with use of (Agilent) PY-2020id/7890A GC/5975c MSD pyrolysis chromatography-mass spectrometry. The pyrolysis system consisted of UA-5 (5%diphenyl) super alloy capillary chromatographic column(30m×0.25mm i.d.×0.25μm). Pyrolysis temperature was 550^0C, carrier gas was helium and carrier gas rate was 50mL/min. Sample (100±10μg) was put in platinum boat and then the platinum boat was put in pyrolyzer. Single-Shot Anacracker lysis of sample was conduct by PY-2020id vertical tube furnace cracker. The sample was pyrolyzed in an inert atmosphere at 550^0C (which maintains for 0.5min.) and then the pyrolysis products were put in gas chromatography system.

UA-5 (5% diphenyl) super alloy capillary chromatographic column(30m×0.25mm

i.d.×0.25μm) was used, and stationary phase material was a weakly polar polymethylphenyl silicone (5%diphenyl).Temperature of injection port of separation column was 320^0C. Course of programmed temperature was: initial temperature 50^0C maintaining 1 min., and then temperature increasing to 320^0C in a rate of 20^0C /min., and maintaining 10 min. Carrier gas was high purity helium. The carrier gas flow rate was 1.0mL/min. Sample split ratio was 50:1. The total run time was 13.5min.

The temperature of GC/MS Interface was 300^0C.Ionization method was EI. Ionizing voltage was 70eV. The temperatures of ion source and quadrupole rods were 230^0C and 150^0C, respectively. Scan rate was 1 Scan/Sec. The range of scan mass number was 35~500 amu. NIST08.L Mass spectrometry library was used to retrieve Ms spectra data.

Py-GC/MS and computer combination instrument were used to separate fragment ions (volatile component after sample pyrolysis) in chromatographic column and then to mass spectrum qualitative. NIST mass spectrometry library was used for retrieve analysis. Relative mass fraction of quantitative data was processed by area normalization method. The composition were determined by mass spectrometry analysis

Results and Discussion

Infrared Spectrum Analysis

Fig.1 is infrared spectrogram of high purity NR and control sample. Fig.1 shows that the absorption peaks near on 3280cm^{-1} and 1540cm^{-1} are stretching vibration absorption peak of N-H group and vibration compound peak of C-N group and N-H group in amide group, respectively, for the control sample. These groups are caused by protein in NR [11]. However, these groups on 3280cm^{-1} and 1540cm^{-1} disappear completely for high purity NR.

Py-GC/MS

Fig.2 is the total ion figure of high purity NR and the control sample pyrolysis at 550^0C.Fig.3 is Pyrolysis chromatogram of high purity NR and the control sample. From Fig.2 and Fig.3, the pyrolysis products and the mass fraction of pyrolysis products of high purity NR and the control sample are obtained according to NIST08.L mass spectrometry library of computer. The results are showed in Table1.

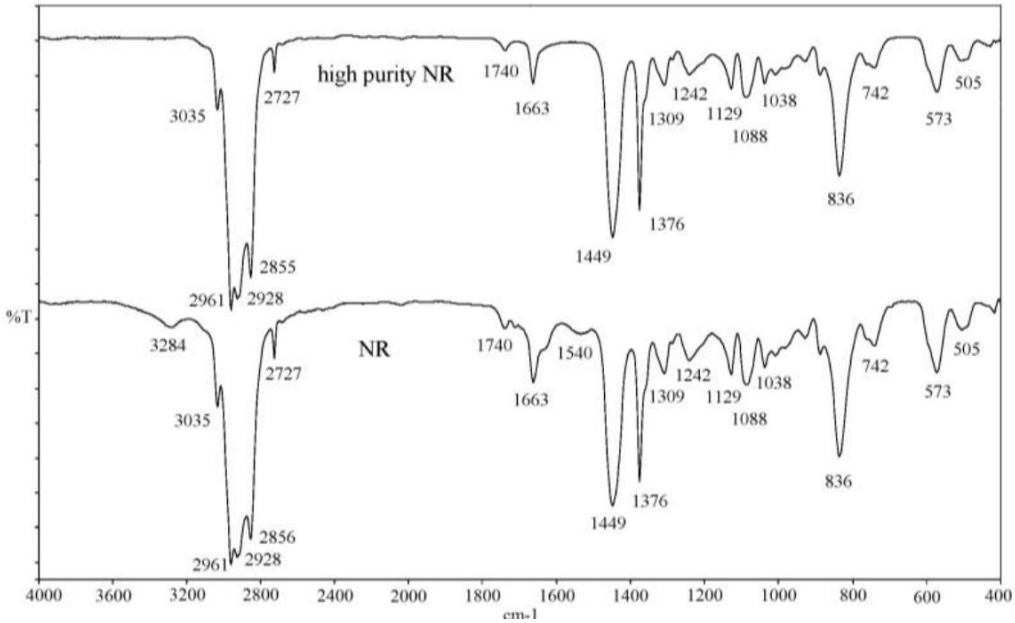

Fig.1 Infrared spectrogram of high purity natural rubber and control sample

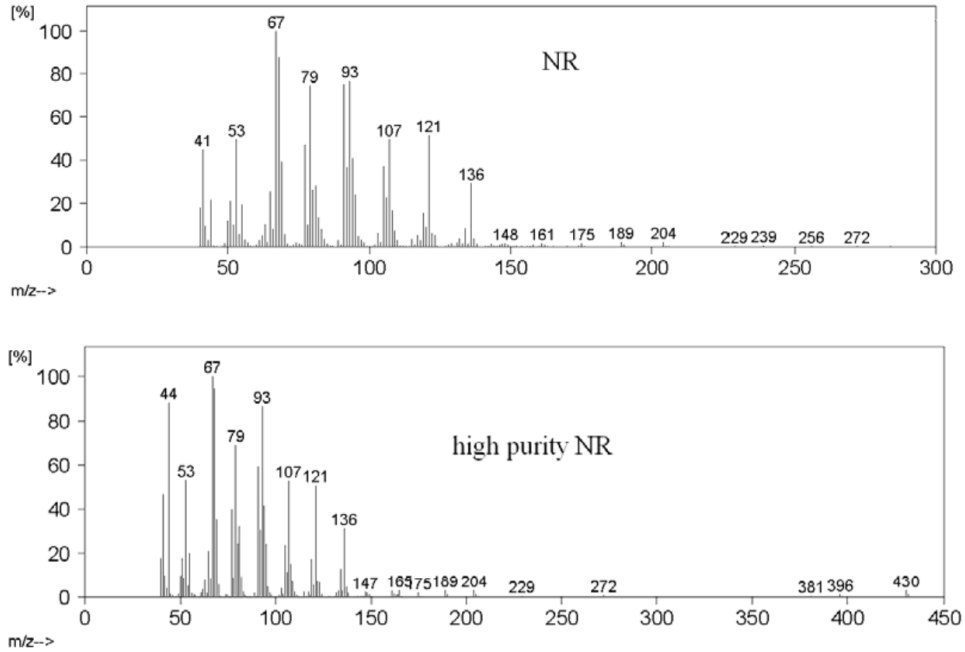

Fig.2 Total ion figure of high purity NR and the control sample pyrolysis at 550^0C

It is known from Table 1 that there are 11 types of pyrolysis products in high purity NR. One of these pyrolysis products is alkyne and others are olefins. The highest levels of three pyrolysis products, in turn, are Limonene, 4-ethenyl-1,4-dimethyl-Cyclohexene and 1,3-Pentadiene.There are 15 types of pyrolysis products in the control sample. Among them, 10 types of pyrolysis products are olefins, 2 types are aromatics, and other three types are alkyne, alkane and condensed aromatic hydrocarbons, respectively. The highest levels of three pyrolysis products, in turn, are limonene, 1, 5, 5-trimethyl-6-methylene-cyclohexene and 1, 3-pentadiene. There appear 2-methyl-1, 3-Butadiene,3-Heptadecen-5-yne, 2,4,6- Trimethyl-1,3,6-heptatriene-(3R-trans) Cyclohexene, 4-methyl-1-(1-methylethenyl)-Cyclohexene, 1,3,8-β-Menthatriene, β-Humulene in pyrolysis products of high purity natural rubber, but above 6 types of compositions do not appear in pyrolysis products of the control

sample. 1,4-Cyclohexadiene, 2-methyl -1,5-Hexadien-3-yne, 1,3-dimethyl-Benzene, cis-2,6-Dimethyl-2,6-octadiene, 8-methylene -Bicyclo[5.1.0]octane, 1,5,5- Trimethyl -6-methylene-cyclohexene, 3-methyl-6-(1-methylethenyl)- (3R-trans)- yclohexene, 1-methyl-4-(1-methylethenyl)-Benzen, 3-ethenyl-1,2 -dimethyl-1,4- Cyclohexadiene appearing in pyrolysis products of the control sample do not appear in pyrolysis products of high purity natural rubber. There are 5 types of compositions, including 1, 3-Pentadiene, 1-methyl-1, 4- Cyclohexadiene, 4-ethenyl-1, 4-dimethyl-Cyclohexene, Limonene and 1-ethenyl-1-methyl-2- (1-methylethenyl)- 4-(1-methylethylidene)-Cyclohexane appear not only in pyrolysis products of high purity natural rubber but also in pyrolysis products of the control sample. Above 5 types of pyrolysis products are all olefins, and are 73.15% of the mass fraction of total pyrolysis productions in high purity natural rubber, 49.04% of the mass fraction total pyrolysis productions in the control sample. It is **i**ndicate**d** that the 5 types of pyrolysis products are predominance in all pyrolysis products of high purity NR and the control sample.

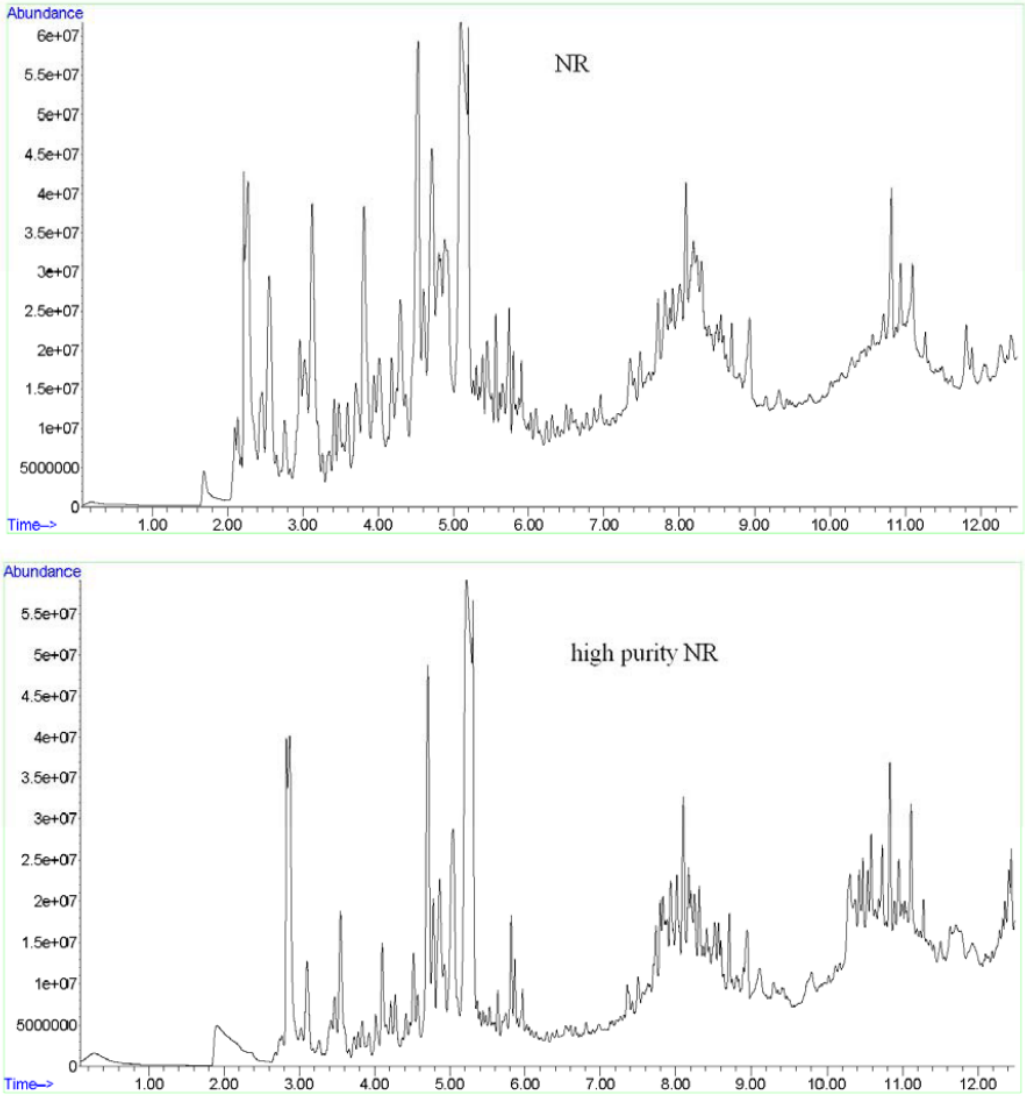

Fig.3 Pyrolysis chromatogram of high purity NR and the control sample

Table 1 Structures and components of fragment ions corresponding each peak in chromatogram of high purity NR and the control sample

Serial number	Compound	Control		High purity NR	
		Respons time /min	Relative amount/%	Response time /min	Relative amount/%
1	2-methyl-1,3-Butadiene			2.833	4.82
2	1,3-Pentadiene	2.221-2.273	11.25	2.874	11.12
3	1,4-Cyclohexadiene	2.553	5.45		
4	1-methyl-1,4-Cyclohexadiene	2.967	3.08	3.550	4.94
5	2-methyl-1,5-Hexadien-3-yne	3.124	6.96		
6	1,3-dimethyl-Benzene	3.818	5.90		
7	cis-2,6-Dimethyl-2,6-octadiene	4.302	4.27		
8	4-ethenyl-1,4-dimethyl-Cyclohexene	4.535	11.11	4.710	11.69
9	8-methylene-Bicyclo[5.1.0]octane	4.605	3.04		
10	1,5,5-Trimethyl-6-methylene-cyclohexene	4.716-4.809	13.89		
11	3-Heptadecen-5-yne			4.780	3.53
12	2,4,6-Trimethyl-1,3,6-heptatriene			4.867	5.93
13	3-methyl-6-(1-methylethenyl)-(3R-trans)-Cyclohexene	4.890	7.20		
14	4-methyl-1-(1-methylethenyl)-Cyclohexene			5.042	9.43
15	Limonene	5.100-5.199	21.83	5.223-5.304	36.17
16	1-methyl-4-(1-methylethenyl)-Benzene	5.561	1.26		
17	3-ethenyl-1,2-dimethyl-1,4-Cyclohexadiene	5.741	1.64		
18	1,3,8-p-Menthatriene			5.817	1.81
19	4α,8-dimethyl-2-(1-methylethenyl)-Naphthalene	8.090	1.34		
20	β-Humulene			8.108-11.116	6.15
21	1-ethenyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-Cyclohexane	10.818	1.77	10.836	4.41

Conclusions

The molecular structure of high purity NR is simpler than that of the control sample, and the pyrolysis productions of high purity NR at 550 ^{0}C are less than that of the control sample. There are 11 types of pyrolysis productions in high purity NR. Limonene, 4-ethenyl-1,4-dimethyl-Cyclohexene, 1,3-Pentadiene are main productions that is 58.98% of the mass fraction of total pyrolysis productions in high purity NR.

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