

**DETERMINATION OF THE CROSS-LINK DENSITY OF VULCANIZED
POLYISOPRENE BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS
SPECTROMETRY ***

DIN XIGAO * and LI HUIMING

Institute of Chemistry, Academia Sinica, Beijing (Peoples Republic of China)

(Received December 3rd, 1980; accepted January 20th, 1981)

SUMMARY

The determination of the cross-link density of vulcanized polyisoprene by means of pyrolysis-gas Chromatography-mass spectrometry was investigated. The main degradation products were isoprene, 1,5-dimethyl-5-vinylcyclohexene, 1-methyl-4-isopropyl-1-cyclohexene (dipentene) and 3-methyl-1,3-pentadiene. The quantitative results indicated that the amounts of monomer and dimer decreased with increasing cross-link density, but the yield of 3-methyl-1,3-pentadiene was independent of the cross-link density. A linear relationship exists between dipentene to 3-methyl-1,3-pentadiene (ratio of the peak areas or peak heights) and the cross-link density. The reproducibility of the results was generally good (the relative standard deviation was less than 2.0%).

INTRODUCTION

The determination of cross-link density is an important parameter characterizing a vulcanized rubber. As vulcanized rubber is an insoluble and non-flowing polymer network, usually containing many additives, conventional analytical methods, such as IR and NMR spectroscopy, are difficult to apply. Although the swelling equilibrium method, based on a firm theoretical foundation, is an important classical method for determining cross-link density, it is time consuming. Determination of the content of combined sulphur is widely used in industry. In this method, the free sulphur must be extracted completely, otherwise considerable errors may result.

In pyrolysis-gas chromatography (Py-GC), a polymer sample is rapidly degraded under specified conditions into smaller molecular fragments, which are then separated and identified by gas chromatography-mass spectrometry (GC-MS) in order to obtain structural information about the sample [1,2]. Cross-linked polymers and composite materials containing additives can also be directly analysed by Py-GC without resorting to elaborate separations.

*Presented at the 29th Annual Meeting of the Japan Society for Analytical Chemistry, Fukuoka, October 11-15, 1980.

Much work on the analysis of the composition and the micro-structure of rubber by Py-GC has been published [1-3], but few studies have been made of the relationship between pyrograms and the cross-link structure of rubber. In this work, we compared the pyrograms of vulcanized polyisoprene with various cross-link densities and analysed the structure and composition of the degradation fragments.

EXPERIMENTAL

Preparation of the samples

Six samples with various cross-link densities were prepared by a conventional method using 1-6% sulphur as the curing agent, and vulcanization was carried out at 143 °C for 40 min. The vulcanized rubber was sectioned into small pieces, extracted with acetone for 8 h in a Soxhlet extractor and dried under vacuum at 40 °C for 24 h. The formulation of the samples is listed in Table 1.

Calibration of the cross-link density was carried out by the swelling equilibrium method.

The densities of the samples were determined by dilatometry. The samples were subsequently kept in benzene for 1 week at 25 ± 0.1 °C in order to reach equilibrium swelling.

Pyrolysis-gas chromatography

A schematic diagram of the equipment used is shown in Fig. 1. It consists of a JHP-2 Curie-point pyrolyser by Japan Analytical Industry (Tokyo, Japan), attached to a Chromatron GCHF 18.3 and/or a Pye Model 104 gas chromatograph with a flame ionization detector (FID). About 1 mg of each sample was pyrolysed for 4 s by using various ferromagnetic foils having different Curie points, ranging from 358 to 920 °C. Other operating conditions are given in Table 2.

Mass spectrometry

The pyrolytic products appearing on the pyrograms were identified with an AEI Model MS 50 mass spectrometer connected with the GC system. The operating conditions are given in Table 2.

TABLE 1

Composition of prepared samples

Curing temperature, 143 °C; time, 40 min.

Component	Weight (g)	Component	Weight (g)
Polyisoprene	100	Pine tar	5
Carbon black	50	Stearic acid	3
Antiager D	22	Accelerator CZ	1
Zinc oxide	5	Sulphur	1,2,3,4,5,6

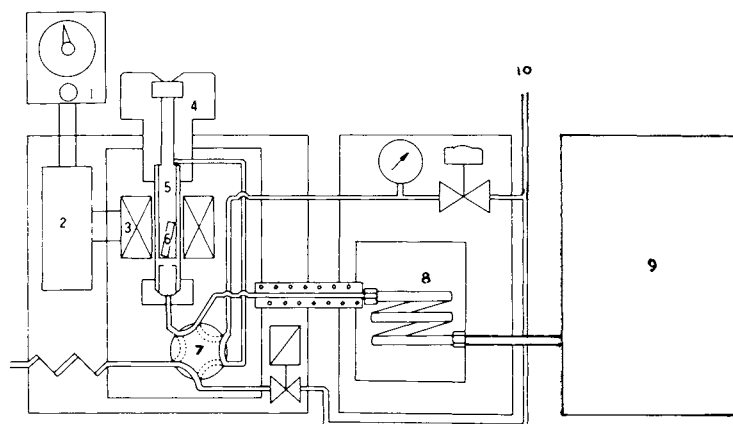


Fig. 1. Flow diagram of Py-GC-MS system. 1, Timer; 2, oscillator; 3, induction coil; 4, injector; 5, quartz tube; 6, sample charge; 7, valve; 8, GC column; 9, mass spectrometer; 10, carrier gas.

Determination of glass transition temperature (T_g) by viscoelastic spectrometry

For determination of the T_g , an Iwamoto Model VES viscoelastic spectrometer was used at a frequency of 3.3 Hz with linear temperature programming at a rate of 2.0 °C/min.

TABLE 2
Operating conditions for pyrolysis-gas chromatography-mass spectrometry

Parameter	Conditions
Sample	ca. 1 ± 0.005 mg
Pyrolyser	JHP-2 (Japan Anal. Ind., 150 W)
Pyrolysis temperatures	358, 434, 590, 650, 764, 920°C
Gas chromatograph	Pye 104 and GCHF 18.3 (Chromatron)
Column	2 m \times 3 mm I.D., packing 15% silicone DC 550 on Chamelite (60-80 mesh)
Column temperature	60-90°C
Carrier gas	Helium and nitrogen, 20 ml/min
Detector	FID, 150°C
Mass spectrometer	MS-50 (AEI)
Resolution	3000
Source temperature	170°C
Electron energy	50 eV
Accelerating voltage	8000 V, 10 in./decade
Surface temperature	130°C

TABLE 3
Analytical data for vulcanized polyisoprene

Sample No.	Yield of pyrolysis products (peak area/mg)				Dipentene: 3-methyl-1,3-pentadiene		$\bar{M}_c \times 10^3$	T_g (°C)	Sulphur content (wt.%)
	Isoprene	Dipentene	3-Methyl-1,3-pentadiene	Peak-area ratio	Peak-height ratio				
1	5.74	19.42	0.75	25.89	6.11	11.4	-56	1.20	
2	4.74	16.31	0.83	19.58	3.40	8.4	-53	1.59	
3	4.31	12.03	0.76	15.74	3.25	7.7	-51	1.77	
4	3.78	9.42	0.74	12.30	2.52	6.9	-49	2.29	
5	2.77	8.81	0.84	10.51	1.87	6.4	-48	2.87	
6	2.04	7.01	0.82	8.51	1.56	5.9	-47	4.82	

Content of combined sulphur

The content of combined sulphur was determined by elemental analysis (barium chloride test).

RESULTS AND DISCUSSION

Calibration of the cross-link density

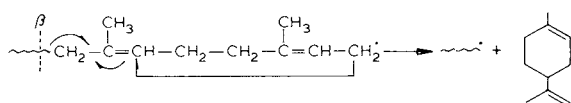
The volume fraction of the polymer after swelling equilibrium was measured, then the average molecular weight between cross-linking points (M_c) was calculated from the values of V_2 according to the Flory-Rehner equation:

$$\ln(1 - V_2) + V_2 + uV_2^2 + \frac{\rho \tilde{V}}{M_c} V_2^{1/3} = 0$$

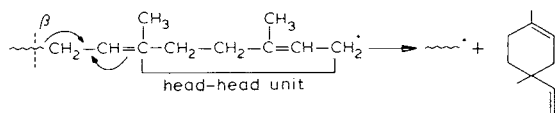
where u is the interaction coefficient of the polymer/solvent system (for natural rubber-benzene, $u = 0.437$), ρ is the density of the sample, \tilde{V} is the molar volume of the solvent (for benzene, $\tilde{V} = 89.3$). The M_c values obtained for various samples are given in Table 3.

Qualitative analysis of Py-GC-MS results

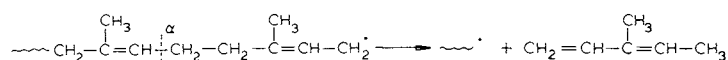
Fig. 2 shows a typical pyrogram obtained from vulcanized rubber that had been degraded at 434°C. There are four major fragment peaks, A, B, C and D, the mass spectra of which are illustrated in Fig. 3. Peak A is monomeric isoprene, B is 3-methyl-1,3-pentadiene, C is 1,5-dimethyl-5-vinylcyclohexene and D is 1-methyl-4-isopropylcyclohexene (dipentene). A simple degradation mechanism which shows that dipentene came from 1,4-1,4 units along the polymer chain is indicated below. We believe that chain scission occurs at the P-carbon atom adjacent to a C=C bond and then cyclization takes place by "back-biting" involving two isoprene units to produce the dimer [4,5]:



Small amounts of 1,2 and 3,4 units, or head-head structural units present in the polymer, may lead to the formation of cyclic dimer C [6-8]:



Another characteristic peak of the pyrolytic fragment, 3-methyl-1,3-pentadiene, was formed via chain scission at an α -carbon atom:



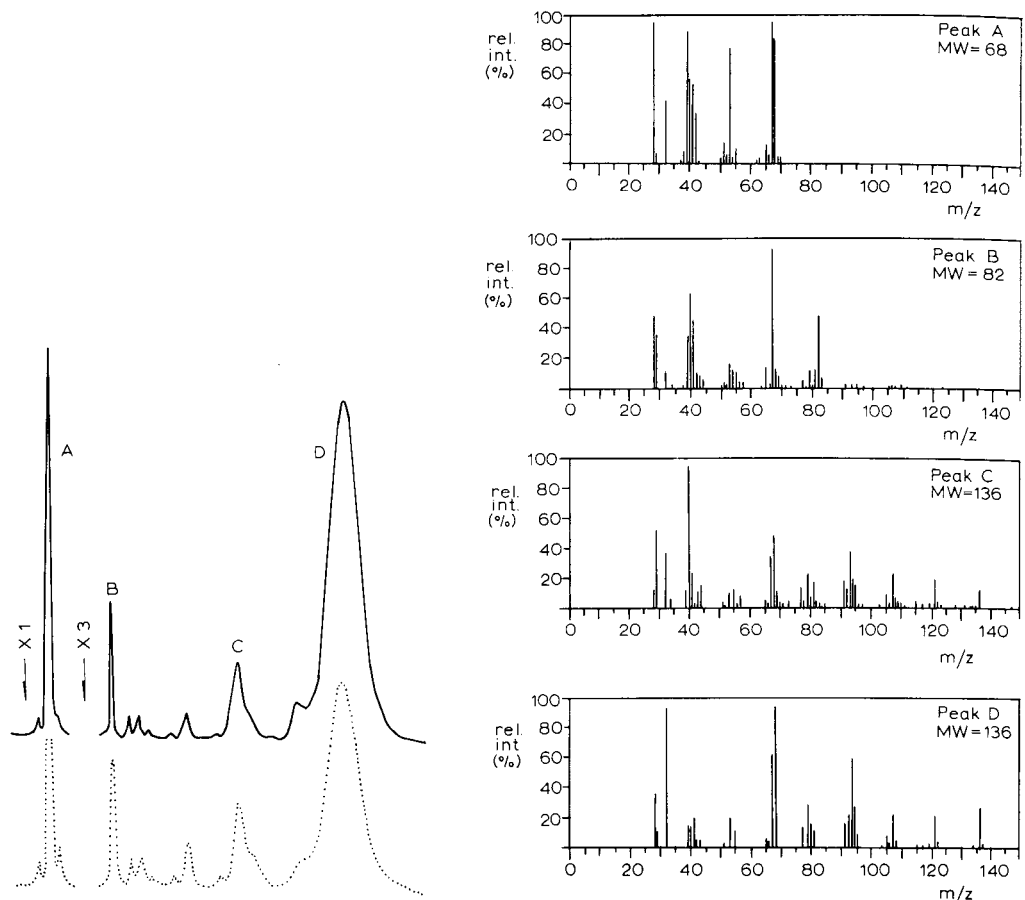


Fig. 2. Pyrograms of vulcanized polyisoprene. \bar{M}_c : —, $11.4 \cdot 10^3$; ·····, $5.9 \cdot 10^3$.

Fig. 3. Mass spectra of degradation products (peaks A, B, C and D from the pyrogram in Fig. 2).

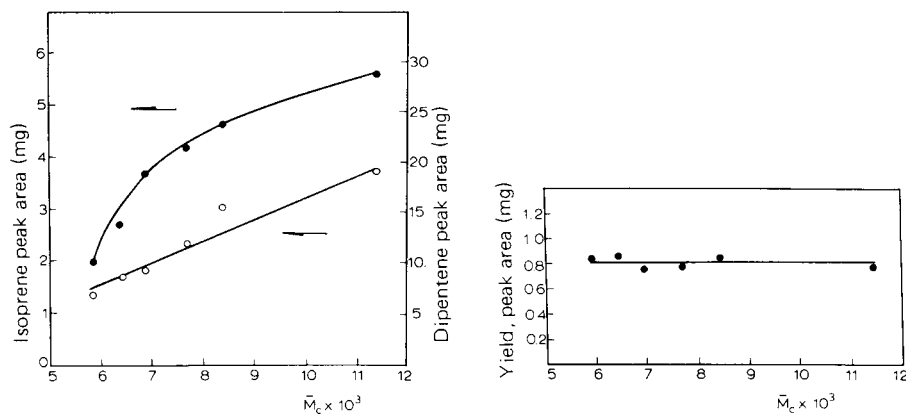


Fig. 4. Relationship between the degree of cross-linking and yield of isoprene and dipentene.

Fig. 5. Relationship between the degree of cross-linking and yield of 3-methyl-1,3-pentadiene.

Of course, the probability of chain scission at an α -carbon atom is much less than that of β -scission, so the yield of B is much less than those of the monomer and dipentene.

Relationship between yield of degradation products and cross-link density

The yields of various degradation products obtained at a degradation temperature of 434 °C were determined (Table 3). The contents of monomer and dimer decrease with increase in cross-link density, and this tendency is greater for the dimer than for the monomer (Fig. 4), because the retro-propagation was retarded by the presence of cross-link sites. For the formation of fragments of higher molecular weight, this effect becomes more pronounced. As the probability of β -scission is much less than that of α -scission, the effect of M_c on the yield of 3-methyl-1,3-pentadiene can be neglected (Fig. 5). For this reason, when the peak-height (or peak-area) ratio of dipentene to 3-methyl-1,3-pentadiene is plotted against the degree of cross-linking, a linear relationship is obtained, as shown in Fig. 6. Py-GC has been used to determine the composition of blended and copolymerized rubber, without considering the effect of cross-link density on the yield of the monomer and dimer. However, as is clearly shown in Fig. 6, the influence of the cross-link density is significant, and should not be neglected, otherwise, considerable errors may be introduced.

Experimental conditions and reproducibility

Experimental conditions such as pyrolysis temperature, temperature rise time, sample size, volume of pyrolysis chamber and other GC conditions, should be carefully controlled in order to obtain high reproducibility in Py-GC. By comparing the yield of dipentene at various temperatures (from 385 to 920°C), we found that the maximal yield of the dipentene peak occurs at 434 °C, where the experimental error in peak area or peak height is minimal (Fig. 7). For Py-GC, the smaller the sample size, the better is the

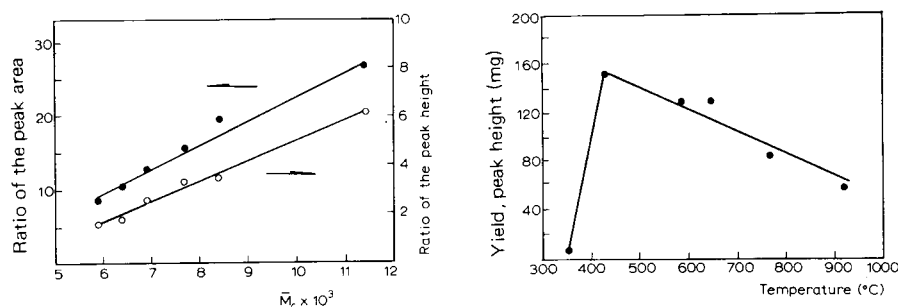


Fig. 6. Relationship between the degree of cross-linking and peak-height and peak-area ratios of dipentene to 3-methyl-1,3-pentadiene.

Fig. 7. Dependence of dipentene yield on pyrolysis temperature.

TABLE 4

Experimental reproducibility

Sample 4 (Table 3).

Peak-area ratio of dipentene to 3-methyl-1,3-pentadiene

Experimental	Average	$\sigma^* = \sqrt{\frac{\sum d_i^2}{N-1}}$	$\sigma^{**} (\%)$
12.07	12.30	0.24	2.0
12.16			
12.69			
12.44			
12.08			
12.34			

* Standard deviation.

** Relative standard deviation.

reproducibility, but owing to the non-uniformity of the industrial rubber sample, 1 mg of sample would be appropriate. The analytical data obtained from sample 4 by using the peak-area ratio of dipentene to 3-methyl-1,3-pentadiene are shown in Table 3. The reproducibility was generally good, with a standard deviation of less than 2% (Table 4).

Comparison with other measurements

Other methods (e.g., swelling equilibrium, dynamic mechanical measurement of T_g and elemental analysis) can be used for the determination of cross-link density. Fig. 8 shows the relationship between \bar{M}_c and T_g as obtained by viscoelastic measurements. However, the relationship is not

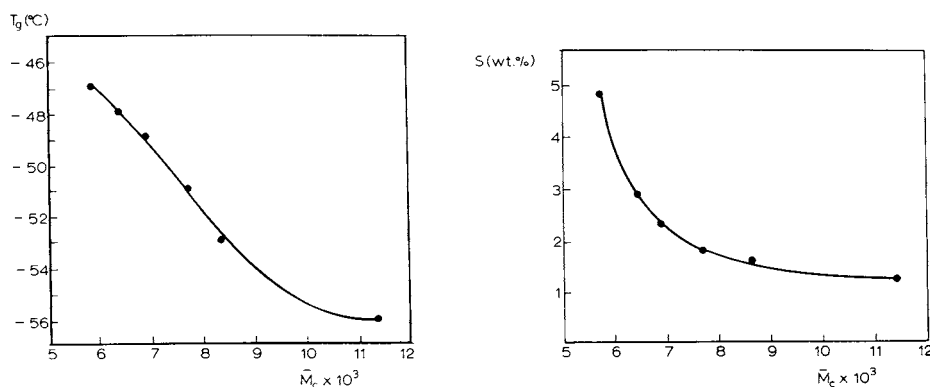


Fig. 8. Relationship between the degree of cross-linking and the glass transition temperature (T_g).

Fig. 9. Relationship between the degree of cross-linking and content of combined sulphur.

linear, in agreement with earlier reports [9]. The relationship between Mc and content of combined sulphur is shown in Fig. 9. It was found that when the content of sulphur is high, the extraction of free sulphur will not be complete, and when the content of sulphur is low the experimental error becomes very large.

The determination of the cross-link density of vulcanized polyisoprene by Py-GC-MS has been demonstrated to be advantageous with regard to simplicity (no pre-treatment is needed) and rapidity (about 15 min for each run), only a small amount of sample is needed and the reproducibility is good.

REFERENCES

- 1 Jin Xigao, *Huaxue Tongbao (Chemistry)*, 1978 (1978) 245.
- 2 T. Takeuchi and S. Tsuge, *Pyrolysis Gas Chromatography of Polymers*, Kagakudogin, Kyoto, 1977, p. 138.
- 3 T. Kono, S. Suzuki and T. Kurihara, *J. Soc. Rubber Ind. Jap.*, 44 (1971) 17.
- 4 M. Galin-Vacherot, *Eur. Polym. J.*, 7 (1971) 1455.
- 5 M.J. Hackathorn and M.J. Brock, *Rubber Chem. Technol.*, 45 (1972) 1259.
- 6 M. Galin, *J. Macromol. Sci., Chem.*, A7 (1973) 873.
- 7 D. Braun and E. Conji, *Angew. Makromol. Chem.*, 29 (1973) 491; 33 (1973) 143.
- 8 A. Krishen and R.G. Tucker, *Anal. Chem.*, 46 (1974) 29.
- 9 H. Kambe, *Thermal Analysis*, Kodansha, Tokyo, 1975, p. 272.