

[CONTRIBUTION FROM THE EASTMAN LABORATORY OF PHYSICS AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

X-Ray Study of Amorphous Rubber

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Introduction

Previous x-ray work on rubber¹ has shown that unstretched rubber gives a distinctly amorphous pattern, while rubber stretched several hundred per cent. gives a typically crystalline pattern. Although considerable work has been done on the interpretation of the x-ray results for stretched rubber, no serious attempt has been made to analyze the amorphous pattern. It is the purpose of this paper to present a Fourier analysis of the x-ray scattering curve for unstretched rubber, and to discuss critically the amount of information concerning the structure of unstretched rubber which can be deduced from the amorphous pattern. By using the new method of Fourier analysis, one gets directly from the x-ray scattering curve the distribution of neighboring atoms about any given atom, without making any *a priori* assumptions as to crystallinity or the nature of the molecule.

Experimental

The diffraction patterns were made in a cylindrical camera of radius 4.40 cm. using $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation. To eliminate background corrections, the radiation was monochromatized by reflection from a rock salt crystal, and the camera evacuated to eliminate air scattering. The sample was a cylinder of smoked sheet² of diameter 1.5 mm. The microphotometer records of the $\text{CuK}\alpha$ and $\text{MoK}\alpha$ patterns were changed to intensity curves in the usual way. The two curves were corrected for polarization and absorption and then fitted together. At small values of $\sin \theta/\lambda$ the Cu curve was considered the more reliable, while at the larger values, the Mo curve showed more detail and was therefore given the greater weight. The final intensity curve, corrected for polarization and absorption, is shown in Fig. 1A, plotted against $\sin \theta/\lambda$.

Fourier Method Applied to Rubber

The application of Fourier analysis to the x-ray scattering patterns of crystalline or non-crystal-

(1) For a summary of the early work, see Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlagsgesellschaft m. b. H., Leipzig, 1930; Katz, "Die Röntgenspektrographie als Untersuchungsmethode," Urban and Schwarzenberg, Berlin, 1934.

(2) We are indebted to D. Kitchin of the Simplex Wire and Cable Company for the raw material.

line materials has been described in previous papers.^{3,4} For a material containing only one kind of atom, the weighted average density of surrounding atoms is given by the relation

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \left(\frac{2r}{\pi}\right) \int_0^\infty s i(s) \sin rs \, ds \quad (1)$$

where $4\pi r^2 \rho(r) \, dr$ is the average number of atoms between r and $r + dr$ from any atom.

ρ_0 = average density of sample in atoms per unit volume.

s = $4\pi \sin \theta/\lambda$

$i(s)$ = $(I/N - f^2)/f^2$

I/N = unmodified intensity per atom in electron units.

f = atomic scattering factor.

The composition of the sample was taken to be C_8H_8 . Relative to the carbon atoms the unmodified scattering from the hydrogens can be neglected. In applying the Fourier method we therefore consider the sample as made up of carbon atoms alone. The unmodified scattering per atom is taken as f_c^2 , and the modified scattering per atom as the modified scattering per carbon plus eight-fifths the modified scattering per hydrogen. The modified and independent unmodified scattering⁵ per carbon atom are given by curves C and D of Fig. 1. The total independent scattering per carbon atom is given by curve B. At large angle the scattering curve of any material approaches independent scattering. The experimental intensity curve A, which is at first in arbitrary units, is therefore drawn to such a scale that it approaches curve B at large angle. This serves to put the experimental curve A upon an absolute basis, electron units per atom. The curve $i(s)$ is then given directly in absolute units by subtracting B from A and dividing through by curve D. The integration involved in equation (1) is readily carried out on the curve $si(s)$ by means of a Coradi harmonic analyzer. Taking the density of unstretched rubber as 0.94 one obtains for ρ_0 the value 0.042 carbon atoms per Å^3 .

The resulting radial density curve $4\pi r^2 \rho(r)$ is given in Fig. 2a. The curve represents the average number of carbon atoms at any distance r from any carbon atom. The area under the

(3) B. E. Warren, *J. Chem. Phys.*, **2**, 551 (1934).

(4) Hultgren, Gingrich and Warren, *ibid.*, **3**, 351 (1935).

(5) From tables of f and Σf^2 in Compton and Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Co., New York, 1935.

curve gives directly the number of carbon atoms in a particular range of distance. Figure 2b gives the differential density, that is, the difference between the actual atomic density and the average density.

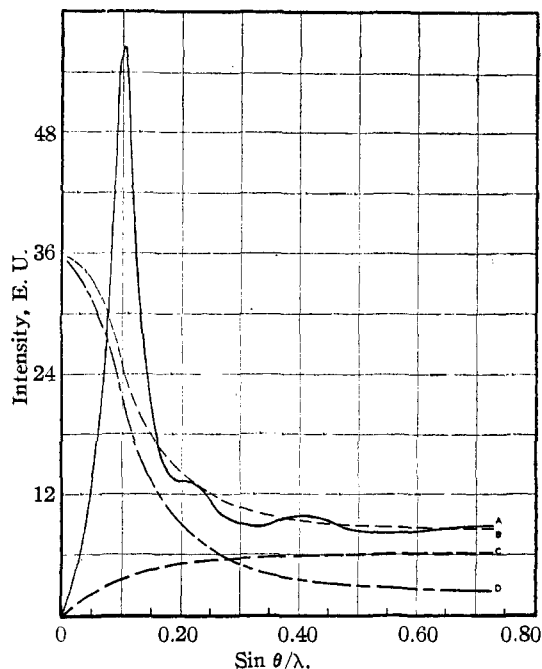


Fig. 1.—A, experimental intensity curve for unstretched rubber; B, total independent scattering per carbon atom; C, modified scattering per carbon atom; D, independent unmodified scattering per carbon atom.

Discussion of Results

From Fig. 2 one finds that on the average each carbon atom in rubber has 1.98 carbon neighbors at a distance of about 1.52 Å. Beyond these nearest neighbors come approximately 3.4 carbon atoms at an average distance of 2.68 Å. Beyond these come further concentrations at about 4.0 and 5.0 Å. It might be pointed out that this much information is obtained directly from the x-ray scattering curve without making any assumptions as to the structure of the sample.

The results are in quite satisfactory agreement with the present picture of rubber as comprised of long chain molecules. Figure 3 represents schematically a section of the chain. The single bond C—C distance is taken as 1.54 Å. and the double bond C—C distance as 1.38 Å. The bond angles are taken as 109°28' and 125°16'. Regardless of free rotation about the single bonds, and consequent bending and coiling of the chain,

the nearest and next nearest neighbor distances are perfectly definite.

TABLE I

FIRST NEIGHBORS		
Atom	No. neighbors and distance, Å.	
1	2—1.54	
2	2—1.54	1—1.38
3	1—1.54	
4	1—1.54	1—1.38
5	2—1.54	

Average 2.0 first neighbors at distance 1.51 Å., in good agreement with the first peak of Fig. 2.

TABLE II

SECOND NEIGHBORS		
Atom	No. of neighbors and distance, Å.	
1	1—2.59	2—2.52
2	1—2.59	1—2.52
3	1—2.59	1—2.52
4	2—2.59	1—2.52
5	1—2.59	1—2.52

Average 2.4 second neighbors at distance 2.56 Å. Of the third neighbor distances the separation between atoms 1 and 5 has the definite value 3.13 Å. The remaining third neighbor distances de-

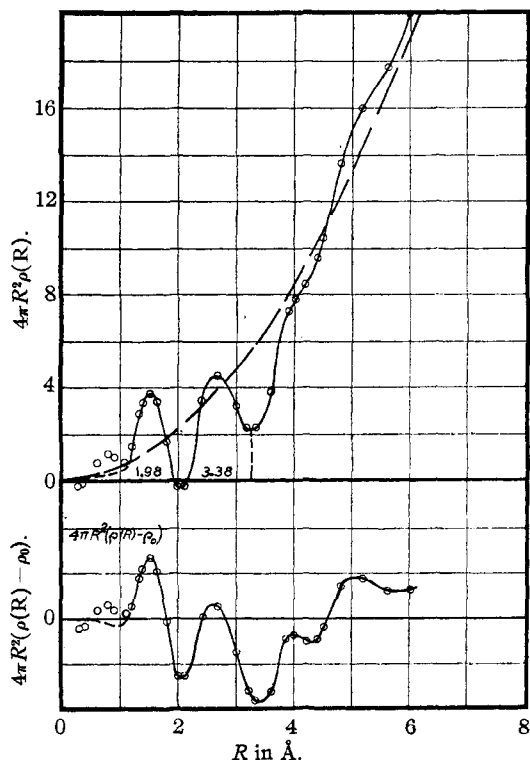


Fig. 2.—(a, upper) Radial density of surrounding atoms in unstretched rubber. (b, lower) Differential radial density of surrounding atoms in unstretched rubber.

pend upon the orientation about the single bond directions, and vary between a minimum of 2.56 Å. and a maximum of 4.04 Å. The second peak of Fig. 2 is only partially resolved on the right-hand side, and therefore includes the 2.4 second neighbors at a distance 2.56 Å. plus the nearest of the third neighbors.

The third peak of Fig. 2 occurring at about 4.0 Å. is evidently due to the more distant third neighbors. The striking correspondence between this peak and the third neighbor peak of a normal hydrocarbon is clearly brought out by comparing Fig. 2b with the density curve for *n*-heptane.⁶ The first three peaks of Fig. 2 are thus completely explained by the usual picture of rubber as comprising long chain molecules.

The fourth peak of Fig. 2 occurs at a little more than 5 Å. This concentration represents an atom's nearest carbon neighbors in other chains, the distance from a carbon atom in one molecule to the first concentration of carbon atoms in neighboring molecules being of the order 5 Å. It may be of interest to point out that it is primarily this concentration of scattering matter which is responsible for the very strong peak at $\sin \theta/\lambda = 0.104$ in the experimental intensity curve. The fact that so many organic liquids such as benzene, cyclohexane, paraffin, rubber, etc., give a strong diffraction ring at just about the same value of $\sin \theta/\lambda$ is simply due to the fact that there is a fairly definite closest distance of approach of carbon atoms in different molecules.

From the analysis of the x-ray pattern of amorphous rubber only two conclusions can be drawn:

1. The x-ray pattern and the resulting density

(6) W. C. Pierce, *J. Chem. Phys.*, **3**, 252 (1935).

curve are completely explained by the usual chain molecule picture of rubber. It is not necessary to make any specific assumptions as to mutual orientation of the chains.

2. Since no assumptions are necessary, it follows that from the analysis of the amorphous rubber pattern one gets practically no information as to relative orientation of the chains or as to whether the individual chains are straight or coiled. Any specific conclusions which have been drawn from the amorphous pattern of rubber as to the configuration of the chains can have but little significance.

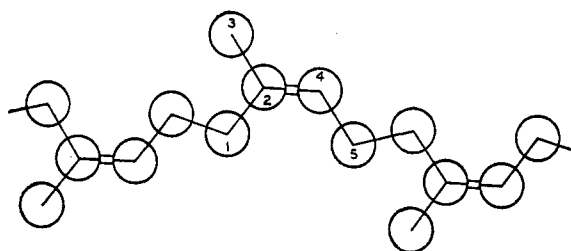


Fig. 3.—Schematic representation of long chain molecule in rubber.

Summary

The density of surrounding atoms in unstretched rubber is determined by a Fourier analysis of the x-ray scattering curve. The resulting distribution curve is in good agreement with the usual picture of rubber as comprised of long chain molecules. It is concluded that but little information can be obtained as to the configuration of the chains in unstretched rubber.

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