THE CONTRIBUTION OF X-RAY RESEARCH TO THE KNOWLEDGE OF RUBBER[1]

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CONTENTS

I. INTRODUCTION

Ever since the observation by Katz, in 1924, that stretched rubber gave x-ray interferences similar to those for a crystalline material, the subject of x-ray diffraction by rubber has been one of continuous interest for research of a fundamental character dealing with the molecular structure of high polymers. At the start, this property of rubber was regarded as more or less individual and distinctive, but in the course of time the tendency has been to show that the behavior of rubber in this respect fits into the general picture of the x-ray diffraction by both natural and synthetic polymers. X-ray diffraction by rubber has thus lost much of its early character as an isolated phenomenon, and its full significance in connection with the general property of high elasticity now can be shown to lie in the quantitative measures of the diffraction and the circumstances, such as the temperature range and elongations, for which various types of diffraction occur.

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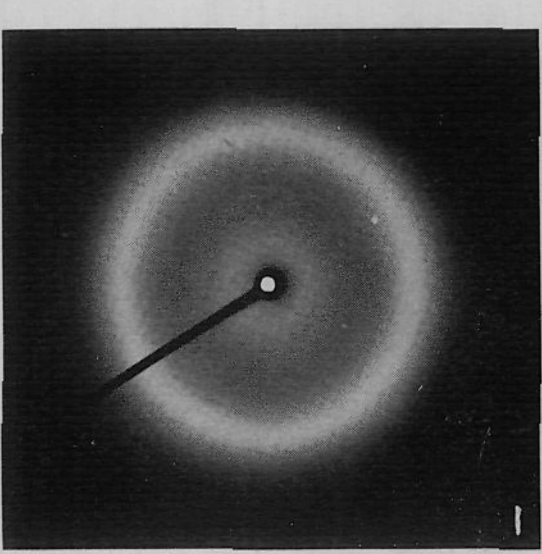
II. CRYSTALLINE AND AMORPHOUS UNSTRETCHED RUBBER

Physical measurements of density, heat capacity, and other quantities associated with changes of form have been interpreted as showing that raw rubber can exist in several modifications, depending upon the temperature. The x-ray patterns sharply distinguish only two modifications: amorphous (60), in which case a pattern similar to that of a liquid is secured, or crystalline, for which a system of Debye–Scherrer rings occurs (55, 40) (see figures 1 and 2). In attempting to fix the transition temperature for these patterns, the situation in regard to the temperature modifications of rubber must be briefly considered.

The duration of the freezing, the pressure, and possibly the temperature during freezing are definitely factors in determining the transition temperature for rubber. If rubber is frozen for a period of several days at a temperature lying roughly between 6°C. and -10°C., it thaws in the range from 6°C. to 16°C. (3).



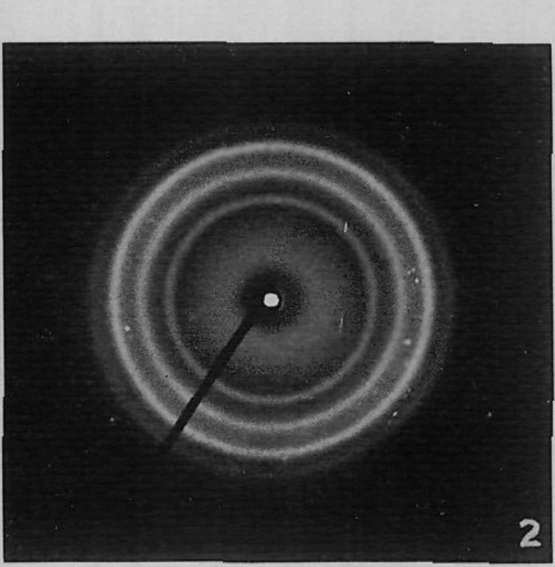


FIG. 1. Pattern for amorphous rubber

FIG. 2. Pattern for frozen rubber

For samples of rubber frozen under pressure, Thiessen and Kirsch (64) found that the crystalline phase was stable up to 20°C., placing the transition point, as determined by x-ray examination, between 20°C. and 23°C. When rubber is frozen for a period of years, it shows a still higher transition point. After being frozen for four years, a sample reported on by van Rossem and Lotichius (58) had a thawing point of 31–33°C.; nine years later this increased to 35–37°C. X-ray diffraction patterns were secured for some of these specimens by Katz (40). In the course of thawing, the Debye–Scherrer rings of frozen rubber gradually become more diffuse and lose intensity. The amorphous halo appears and increases in intensity, its superposition causing a shift in the relative intensity of the Debye–Scherrer rings. Finally, the amorphous halo alone remains. These changes were studied photometrically by Katz. The transition region determined by the disappearance of the crystalline interferences coincided very closely with that determined by the physical measurements, the crystalline interferences becoming imperceptible shortly before the thawing was completed, as is to be expected.

Meyer, v. Susich, and Valkó (52) placed the x-ray transition point even higher, at 35–45°C. Whitby (68) reports a transition temperature, determined by physical means, of 43.5°C. for a sample of rubber believed to have been frozen for thirty years.

The fact that specimens of frozen rubber with thawing points ranging from 8°C. to 43.5°C. all give the same x-ray interferences, differing perhaps in intensity and sharpness, indicates that these various forms represent stages in the exceedingly slow but continuous approach to a stable equilibrium condition rather than distinct modifications. Expressed in terms of the mechanism of crystallization in ordinary liquids, the molecular mobility in rubber at low temperatures must be very small, leading to a low velocity of crystallization. The other factor affecting the speed of crystallization is the rate of formation of nuclei. Owing to the interaction of these factors, the occurrence of crystallinity in rubber proceeds with reasonable speed in a temperature range limited to about +8°C. to −35°C. If the temperature is lowered through this range before the crystallization process is complete, which evidently requires a period of years, the rubber exists in a supercooled state, stable at the lower temperature for all practical purposes. Thus, Pummerer and v. Susich (57) found that rubber held at −190°C. for 8 days gave an amorphous x-ray diagram. This is a notable example of the lack of correlation which can exist between the x-ray diagram and the physical properties.

Bekkedahl (3) found a second transition for both crystalline and amorphous rubber at −72°C. This transition has not been reported in x-ray work, and it is doubtful if it would be perceptible except possibly by photometric measurements of the Debye–Scherrer rings or the halo, respectively.

High pressure has been reported to prevent the crystallization of rubber in the usually favorable range of temperature. In an experiment by Dow (16) crude rubber was held at a pressure of 8000 kg. per cm.^{2} at 0°C. for a period of 14 days, but no evidence of freezing was obtained. This was attributed to the high viscosity induced in the rubber by the pressure. Thiessen and Kirsch (64), on the other hand, working in a lower pressure range of 10 to 25 atmospheres, found that at a given temperature, the higher the pressure, the shorter the time required for crystallization. The application of pressure also enabled crystallization to occur at higher temperatures than would have been otherwise possible. Under a pressure of 25 atmospheres crystallization took place at 10°C., but 15 atmospheres was sufficient to bring about crystallization only at 8°C., as determined by x-ray examination. Comparing the results of Dow with those of Thiessen and Wittstadt, there is evidently a favorable range of pressure for the crystallization of rubber as well as a favorable range of temperature.

The question now arises as to whether the crystalline or amorphous form of rubber is the stable one under ordinary conditions. The thawing points of old samples of frozen rubber are so high as to indicate that this is the stable form, although there is a possibility that the thawing points might be somewhat lower if the thawing process, as the freezing, were of long duration. Crystallization at room temperatures proceeds so slowly, presumably owing to the slow rate of formation of crystallization nuclei, that for all practical purposes the supercooled amorphous form is also stable. Thus amorphous patterns are the general rule for crude rubber under ordinary circumstances. A number of observers have reported the occurrence of crystalline interferences, especially for crepe rubber (42, 57), but it is doubtful if these represent crystallization at room temperature rather than a persistence of crystallization which occurred in the favorable range of temperature.

In general, unstretched vulcanized rubber gives the amorphous halo under all conditions. But vulcanization can be carried out to various degrees, and, presumably, lightly vulcanized samples might be induced to crystallize. The occurrence of the three-dimensional network of primary valence linkages in vulcanized rubber evidently interferes with the movement of the molecules into a crystal lattice to such an extent that crystallization cannot occur spontaneously. In contrast, rubber which has been milled or masticated freezes readily.

III. THE X-RAY DIFFRACTION PATTERN FOR AMORPHOUS RUBBER

In some of the earlier work, rubber was reported to give two halos corresponding to spacings of 6.03 Å. and 14.88 Å. (8, 28). Katz, however, consistently reported the pattern to be a single halo (36, 41). The above values were computed from a formula due to Ehrenfest, which gave somewhat higher values than the Bragg relation now generally used for this purpose. The larger spacing is not mentioned in later work, in which the pattern is regarded as consisting of a single halo corresponding to a spacing usually given as between 4.5 and 4.7 Å. (2, 10, 48). Mark and v. Susich, in photometering the pattern, found a weak halo corresponding to a spacing of 8 Å. This also has not been verified, and in view of the work of Simard and Warren (61), using strictly monochromatic radiation, it appears that these larger spacings which have been reported may have been spurious effects due to continuous background or other causes. With filtered Cu K_α radiation a considerable amount of blackening usually occurs in the central region of the diagram. Further tests with monochromatic radiation are desirable to check this point.

Unstretched vulcanized rubber gives a halo which, as far as is known, is identical with that for unvulcanized rubber. There is some evidence, however, that the halo decreases in diameter as vulcanization proceeds to a stage approaching ebonite (43), showing the occurrence of slightly larger intermolecular spacings. Rubber which has become hard and brittle, owing to oxidation, is also amorphous. Purified sol and gel rubber both give the same halo characteristic of total rubber (12). In addition, for gel rubber Clark observed a large spacing of 54 Å.

The same pattern thus persists in the various forms of amorphous rubber and is indicative of a structure which must resemble that of a liquid in many respects. Katz (41) carried out extensive comparative studies of the patterns of liquids before and after polymerization, in order to reach a better understanding of the meaning of the pattern for rubber. In the case of isoprene and the butadienes, he found that the patterns of the monomers and polymers were identical. Thus, the long chain molecules formed during polymerization and existing in natural rubber assume a short-range structure similar to that in an ordinary liquid. This essentially liquid structure in unstretched, amorphous rubber is frequently lost sight of in attempts to explain the properties of rubber on a mechanical molecular basis. It is, however, one of the most certain features of the molecular structure in rubber.

Simard and Warren (61) have carried through for the pattern of unstretched rubber the same type of Fourier analysis which has been so useful for investigations of the structure of liquids and of glasses. This analysis gives directly from the x-ray scattering curve the radial distribution of neighboring atoms about any given atom without any assumptions in regard to the structure. The results showed that each carbon atom has on the average 1.98 carbon neighbors at a distance of 1.52 Å. Beyond these nearest neighbors are approximately 3.4 carbon atoms at an average distance of 2.68 Å. Further concentrations occur at about 4.0 and 5.0 Å. These results were considered to be in good agreement with a structure composed of long chain molecules, such as is now usually assumed for rubber, using accepted values of the bond lengths and angles. The first three concentrations represent successively remote neighboring atoms in the chain. The concentration at 5 Å. corresponds to an atom's nearest neighbors in other molecules and represents the fairly definite distance of closest approach for carbon atoms of different molecules, such as is observed for many organic liquids. This concentration gives rise to the main peak in the diffraction pattern, and the above distance coincides with the spacing as determined by the application of Bragg's law.

It follows from this work that the diffraction pattern for amorphous rubber offers no features which can give information as to the relative orientation or form of the chain molecules (see figure 3). The superficial resemblance of the pattern to that for a liquid is thus borne out by the analysis. The liquid structure must be reconciled in some way with the existence of the long chain molecules, which are held responsible for the profound difference in the physical properties as compared to liquids. In the case of stretched vulcanized rubber, a tendency of the amorphous halo to split into two equatorial arcs has been observed (34, 43). This can be interpreted as evidence of the alignment of the long chain molecules in the direction of stretching.

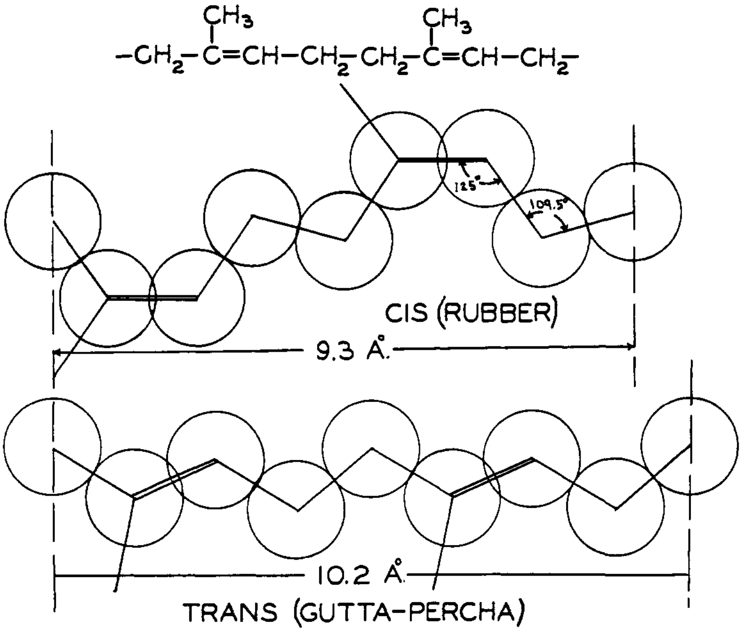


FIG. 3. Planar forms of the rubber chain molecule

IV. THE X-RAY DIFFRACTION PATTERN FOR FROZEN RUBBER

Independent measurements of the spacings for the diagram from frozen rubber are in good agreement, despite a wide variation in the type of specimens. Measurements by Barnes (2) on the patterns for two samples of rubber, one smoked and the other unsmoked sheet which had been frozen over a period of years, and those by Clark, Wolthuis, and Smith (12) on patterns for purified sol, gel, and the total rubber are given in table 1. As no significant differences were found for sol, gel, and total rubber, the values reported for each have been averaged together. Older measurements by Ott (55) for frozen crepe rubber are also in fair agreement, although not as complete.

To all appearances the pattern for frozen rubber resembles that obtained from powdered organic crystals. It shows a structure of minute crystallites in random arrangement. Because of the insolubility of gel rubber, it might be suspected that this material contains primary valence cross-linkages. The crystallization observed may be interpreted as showing that any such network must be an extremely loose one.

TABLE 1

Spacings for frozen rubber

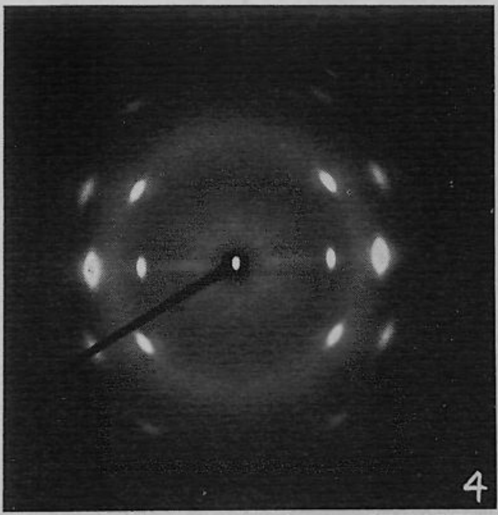
d*	INTENSITY*	d†	INTENSITY†
Å.		Å.	
6.26	s	6.18	s
		5.51	mw
4.97	vs	4.97	s
4.21	vs	4.24	vs
		4.13	
3.74	s	3.70	ms
3.41	m	3.46	m
3.02	wm	3.03	
2.78	w	2.82	
		2.73	w
2.58	m	2.55	
2.41	vw	2.38	vw
2.23	wm	2.21	
2.07	wm	2.07	
1.93	w	1.96	w
1.84	vw	1.83	w

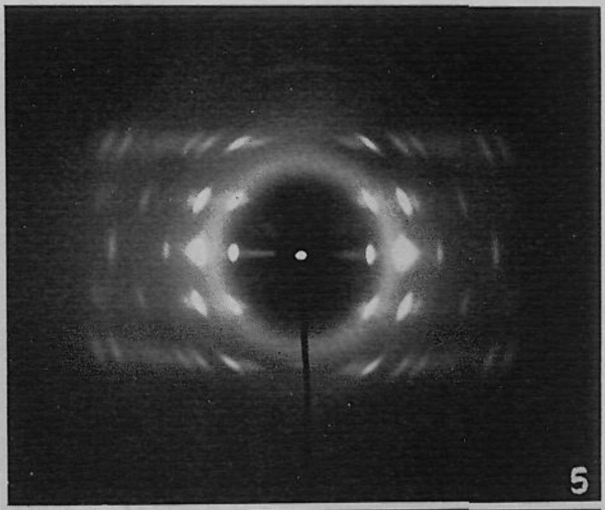
* Measurements by Barnes (2).

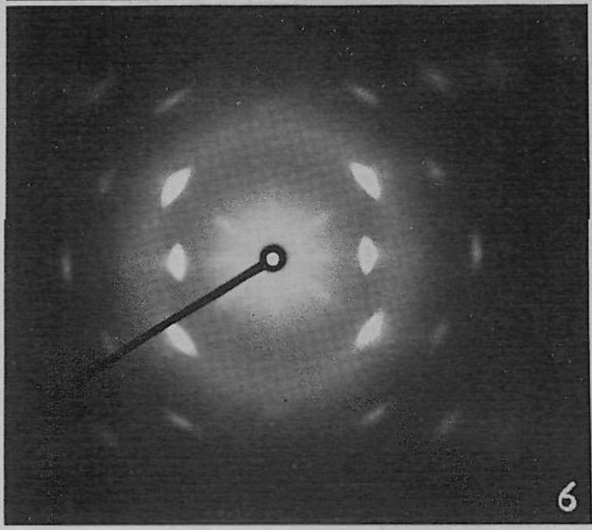
† Measurements by Clark, Wolthuis, and Smith (12).

V. THE X-RAY DIFFRACTION PATTERN FOR STRETCHED RUBBER

The most striking aspect of x-ray diffraction by rubber is the fact, first observed by Katz (36, 38, 39), that when rubber is stretched beyond a critical elongation it gives a fiber diagram with the spots arrayed as in the rotation diagram of a crystal, the axis of rotation corresponding to the direction of stretching (see figures 4 and 5). These diffraction spots appear superposed on the amorphous diagram. They increase in intensity, and the halo decreases in intensity, as the stretching proceeds. The pattern has been substantiated for a wide variety of rubbers from different sources (25, 11). It also generally occurs for rubber purified by diffusion (56, 67), although the sol rubber prepared at the Bureau of Standards and investigated by Clark (12) did not show a fiber diagram at room temperature.







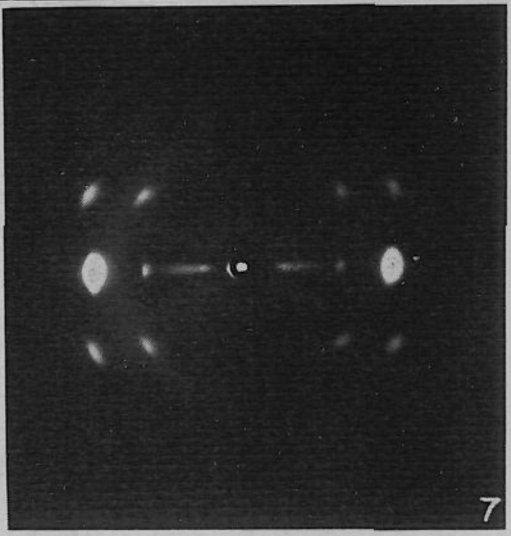


Fig. 4. Pattern for stretched rubber

Fig. 5. Pattern for racked rubber (cylindrical camera)

Fig. 6. Pattern for stretched rubber with higher orientation; beam perpendicular to plane of sheet

Fig. 7. Pattern for stretched rubber with higher orientation; beam parallel to width of sheet

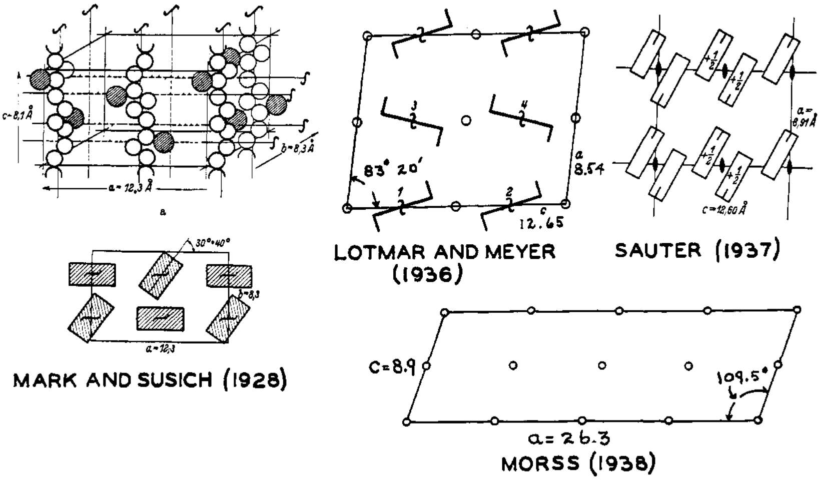
For this material, presumably rendered too plastic by the purification process, a fiber diagram would probably have been obtained at a somewhat lower temperature. This view is supported by the fact that crystallization occurred both upon freezing and when the plasticity was reduced by vulcanization. Evidence is accumulating that the use of ethyl ether as the diffusion medium in the preparation of sol rubber is objectionable (22, 54, 44). Pummerer used ethyl ether but did not claim to observe any significant difference in the x-ray patterns of sol and gel rubber. Nevertheless, it is apparent from the text that some difficulty was experienced in securing the pattern for this sol rubber. When sol rubber is prepared by diffusion in petroleum ether, which may be regarded as a solvent representative of light hydrocarbons, fiber patterns are readily obtained at elongations comparable with those required for latex films. In view of these facts, any conclusions about the structure of rubber based on a qualitative difference between the x-ray behavior of the sol and gel fractions seem unwarranted.

The straightforward interpretation of such a fiber diagram is that crystallites are present which are aligned with one axis in the direction of stretching, the other two axes being in random orientation. It has been shown (55, 2, 12) that the lattice spacings for the Debye–Scherrer rings of frozen rubber agree exactly with those for stretched rubber, proving that the randomly oriented crystallites have the same crystal structure as those in stretched rubber. The lattice spacings depend upon the temperature to an extent determined by the thermal coefficients of expansion, which have been determined in this way (51).

The determination of the lattice in the crystallites and the structure of the unit cell from the fiber diagram has proved to be a difficult problem. Hauser and Mark (27) attempted to index the diffraction spots, but intensity relations discovered subsequently caused the early abandonment of these indices. Later attacks on the unit cell have followed the lines laid down in the investigation of Mark and v. Susich (48).

Mark and v. Susich showed that for stretched films of rubber characteristic changes in the intensity of the diffraction spots occurred, depending upon whether the direction of the x-ray beam was perpendicular or parallel to the plane of the film (see figures 6 and 7). Notably, the first equatorial spot was practically absent when the beam was parallel to the film. The second equatorial spot, on the other hand, was extinguished when the beam was perpendicular to the plane of the film. Rotation of the film gave the normal diagram. The conclusion drawn from these relationships was that the crystallites in the stretched films had all three axes aligned so as to give in effect the structure of a single crystal. Such specimens are said to show "higher orientation." The conditions of stretching necessary to produce higher orientation were studied by Gehman and Field (24). Higher orientation was found to occur when the stretching was carried out in such a way that the per cent contraction in gauge exceeded the per cent contraction in width. This can be readily accomplished by using short, wide sheets of rubber.

The interpretation of the results of Mark and v. Susich was that the first two equatorial spots, designated as A_1 and A_2, arose from families of planes which were essentially perpendicular to each other. This led to the assumption of an orthorhombic lattice, the A_1 spot being indexed as (200) and the A_2 spot as (020). Four long-chain molecules were pictured as traversing the cell in the direction of the fiber axis. From the absence of diffraction by the planes (100), (010), and (001) in uneven orders it was concluded that twofold spiral or screw axes pass through the crystallites in all three directions, leading to the selection of the space group V^4. The twofold spiral axes were explained as arising from the *cis*-form of the hydrocarbon chain (see figure 8), alternate isoprene residues being turned at 180°.



MARK AND SUSICH (1928)

LOTMAR AND MEYER (1936)

SAUTER (1937)

MORSS (1938)

FIG. 8. Base planes of proposed unit cells

There were several discrepancies in this analysis. The density can be calculated from the unit cell by use of the formula

$$d = \frac{1.65Mz}{V}$$

where d is the density in grams per cubic centimeter, M is the molecular weight of the repeating group in the chain molecule, z is the number of such groups in the unit cell, and V is the volume of the cell in Å.^{3}

The density so calculated was about 1.08 as compared to the highest measured value, obtained by stretching and freezing, of 0.965. The A_4 equatorial reflection, assigned indices of (040), did not conform to the lattice. The fiber identity period was too small to accommodate the two isoprene groups of a zigzag planar hydrocarbon chain molecule such as was assumed.

Lotmar and Meyer (46), recognizing these difficulties, undertook a redetermination of the structure by means of a graphical evaluation of the fiber diagram. In this way the A_4 equatorial spot was indexed as (304), which served to determine the axial angle of a monoclinic cell. The twenty-three lattice spacings measured agreed well with those calculated for the cell. These results are given in table 2.

TABLE 2

X-ray interferences of stretched rubber (Lotmar and Meyer)

DESIGNATION OF SPOT	INDICES *hkl*	SPACING	INTENSITY	$\frac{\sin\theta}{\lambda}$ (MEASURED)	$\frac{\sin\theta}{\lambda}$ (CALCULATED)
		Å.			
A_1	(002)	6.29	s	0.079	0.079
A_2	(200)	4.24	vs	0.118	0.118
A_3	(004)	3.14	w	0.159	0.159
A_4	(304)	2.23	vw	0.224	0.224
I_1	(111)	5.50	vw	0.091	0.090
I_2	(012)	5.00	s	0.100	0.100
I_3	(210), (013), (211)	3.76	fs	0.133	0.133, 0.134, 0.134
I_4	$(21\bar{1})$, (212)	3.45	w	0.145	0.142, 0.147
I_5	(114)	2.86	vw	0.175	0.174
I_6	(312), (311), (214)	2.58	w	0.194	0.195, 0.195, 0.196
II_0	(020)	4.10	m	0.122	0.122
II_1	(120), (121)	3.70	w	0.135	0.135, 0.139
II_2	$(12\bar{1})$, (022)	3.45	m	0.145	0.143, 0.145
II_3	(220), (023), (221)	3.01	w	0.166	0.170, 0.170, 0.171
II_4	$(22\bar{1})$, (222)	2.78	w	0.180	0.177, 0.181
II_5	$(22\bar{2})$	2.56	vw	0.195	0.193
II_6	(124)	2.39	vw	0.209	0.209
II_7	(224)	2.20	vw	0.227	0.223
II_8	$(22\bar{4})$	2.08	w	0.240	0.242
II_9	(421), (420)	1.92	vw	0.260	0.264, 0.265
III_1	(130), (131)	2.58	vw	0.194	0.192, 0.195
III_2	(230), (231)	2.29	vw	0.218	0.217, 0.219
III_3	(034)	2.06	vw	0.243	0.242

The density calculated from the cell of Lotmar and Meyer is 1.02. This represents an improvement over the value from the cell of Mark and v. Susich, but it is still high. As shown by Smith and Saylor (62), a density of 1.02 for completely crystallized rubber implies that only 45 per cent of the rubber is crystallized in a sample of density 0.965, taking the density of amorphous rubber as 0.92. Although the presence of some amorphous rubber, even in highly stretched rubber, is indicated by a faint halo, such a proportion seems unreasonable unless the amorphous rubber exists in a form which does not give rise to the characteristic halo. Meyer and Mark (50) judged that at least 80 per cent of the rubber in the extended form was crystallized.

Lotmar and Meyer assumed a spatial or three-dimensional chain form, the exact shape of which was considered to be not yet definitely established. For the cell proposed, four primary valence chains passed through the cell in the direction of the fiber axis, each a spiral with a definite direction of rotation due to the positioning of the isoprene residues. The chains were considered to be alternately stereoisomeric right-hand and left-hand chains. The reflections and extinctions led to the deduction of the space group C_{2h}^5.

Sauter (59) claimed to show that the unit cell of Lotmar and Meyer was impossible. Working with racked samples showing higher orientation, the A_4 interference did not occur at an angle of about 45° to the direction of the A_1 and A_3 reflections in his goniometer pattern obtained when the x-ray beam traversed the sample in the direction of the fiber axis. But the interferences for the axial pattern were long arcs, and Mark and Meyer (47) have disputed his contention. Sauter deduced an orthorhombic unit cell. He considered that the strong equatorial A_2 spot was a double spot, which he indexed as (002), (300). This results in a larger volume for the unit cell and a calculated density of 0.974. Sauter did not give indices except for the equatorial spots, so that the fit of the cell for all the interferences was not submitted.

Morss (53) has reported measurements of about forty lattice spacings, obtained with a cylindrical camera. The results are expressed in coördinates of the reciprocal lattice and greater relative than absolute accuracy was claimed. The ξ values are larger than those calculated from the data of Lotmar and Meyer or Sauter. The cell of Lotmar and Meyer fitted this data well, with the exception of two interferences for which the discrepancy appeared somewhat greater than the probable error of measurement. The planar indices used in the comparison of the cells are not given. Morss regarded this discrepancy as sufficient reason for the rejection of the cell of Lotmar and Meyer. He proposed a monoclinic cell of his own, which, using the data of Lotmar and Meyer to secure absolute values of the lattice spacings, gives a calculated density of 0.965. Morse considered that the work of Mark and v. Susich did not establish that A_1 and A_2 were diffractions by perpendicular families of planes.

These various unit cells are compared in table 3. The base planes of these cells, containing the axes perpendicular to the fiber axis, are represented in figure 8.

The unit cell of Mark and v. Susich has obviously been the starting point for the deduction of all these cells. The question remains as to whether these attempts at refinement have yet reached the truth. It is very doubtful if the unit cell proposed by Sauter can be maintained. It is based on the proposition that the strong equatorial spot A_2 is a double spot. No photometric evidence for this has been offered. Furthermore, it is possible to prepare samples showing higher orientation to such a degree that the intensity of the A_2 spot, (002) by Sauter's indices, can be reduced to a value less than 1 per cent of its normal value as compared to A_1. This small residual intensity, even if due entirely to a (300) interference, would not be sufficient to change the measurement of the spacing for the A_2 spot to the extent required for the Sauter cell.

The use of a monoclinic cell, suggested by Lotmar and Meyer, has undoubtedly brought about an improved agreement with the data. This is to be expected, since there are so many more interferences from which to choose for a monoclinic as compared to an orthorhombic cell, and the number of diffraction spots in the diagram is so limited. Critical tests such as those proposed by Sauter are therefore especially desirable for a monoclinic cell, and the outcome of a number of such independent experiments may very well be capable of giving a definite verdict. In this connection the diagram shown in figure 9 is of interest. This was obtained with the x-ray beam passing in the direction of stretch through a frozen sample showing higher orientation. A more elegant technique for securing suitable samples for this experiment is to vulcanize the stretched sample in sulfur chloride vapor. The structure is retained when the sample is removed from the clamps. The A_2 interference in figure 9 shows two distinct maxima at an angle of about 20° with the equator. The simplest interpretation of this is to regard it as evidence for a monoclinic cell. Accurate measurement of the angle is difficult, owing to the fact that the interferences still overlap in the best patterns which we have been able to obtain.

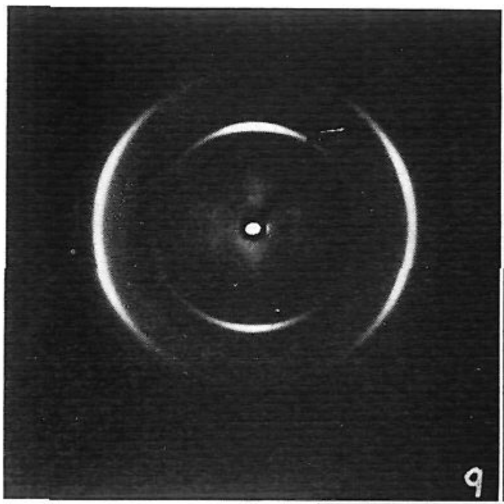
TABLE 3

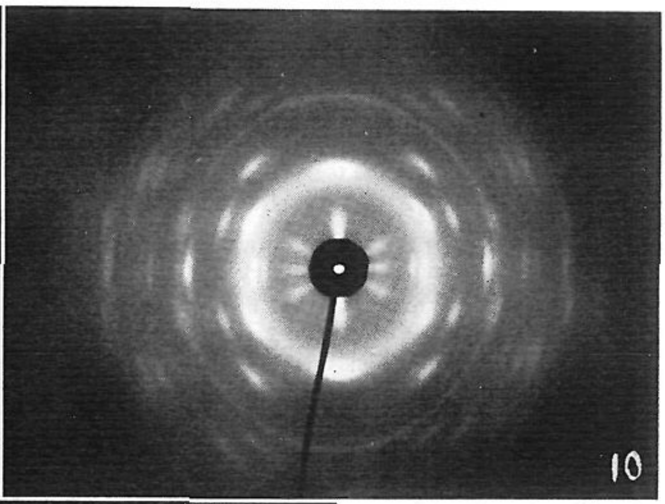
Comparison of various unit cells proposed for stretched rubber

SPONSOR	CLASS	DIMENSIONS			MONOCLINIC ANGLE	CALCULATED DENSITY
		a	*b*	*c*		
		Å.	*Å.*	*Å.*		
Mark and v. Susich	Orthorhombic	12.3	8.3	8.1 (f.p.)		1.08
Lotmar and Meyer	Monoclinic	8.54	8.20 (f.p.)	12.65	83° 20′	1.02
Sauter	Orthorhombic	8.91	8.20 (f.p.)	12.60		0.974
Morss	Monoclinic	26.3	8.15 (f.p.)	8.9	109° 30′	0.965

The artificial aspects of fitting a cell to the data are well brought out by the investigation of Morss. A monoclinic cell arrived at by a systematic variation of the monoclinic angle in a range of values from 90° to 115° was consistent with the diffraction data but was not considered really satisfactory because of the large number of possible diffractions as compared to the moderate number of spots observed. A smaller orthorhombic cell was found in the same investigation which accounted for all but one weak spot.

This apparent inadequacy of the diffraction data to lead to the unambiguous deduction of a unit cell may ultimately be resolved by independent information, such as an improved knowledge of the structure of chain molecules. After all, the fitting of the diffraction spots to a space lattice is not an end in itself but is only one step in determining the structure of the chain molecules and their mutual packing. If more definite limitations in these respects could be imposed, the selection of the cell might become unique.





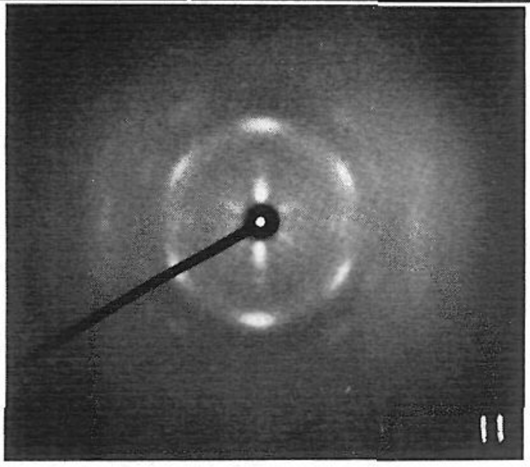


FIG. 9. Frozen sample; higher orientation; x-ray beam parallel to direction of stretch
FIG. 10. Pattern for racked rubber hydrochloride (cylindrical camera)
FIG. 11. Pattern for racked rubber hydrobromide

The value of the fiber period has already shown that the chain molecules in the crystallites of stretched rubber are not planar, a conclusion on which there now seems to be general agreement. Sauter (59) has discussed various chain forms and the possibility that the symmetry of twofold spiral axes, such as is indicated by the extinctions of the diagram, exists not in the individual valence chains but because the chains are displaced by half the fiber period with respect to each other in such a way as to result in the densest packing. He has pointed out that the chain form is determined by the primary-valence field of force and the lattice forces. On this ground he regarded the digonal chain molecules as improbable. Comparative studies of chain forms will undoubtedly be of great assistance in determining the structure of the unit cell for rubber. Lotmar and Meyer (46) called attention to the fact that, owing to the possibility of rotation about the single bonds, the chain structure is not definitely established from the x-ray data even if recognized atomic distances and valence angles are retained.

TABLE 4

X-ray diffraction data for racked rubber hydrobromide

$\lambda = 1.54$ Å.

SPOT	θ	SPACING	INTENSITY
	degrees	*Å.*	
A_1	7° 3.5′	6.27	m
A_2	8° 8′	5.44	m
A_3	14° 15′	3.12	w
I_1	9° 26′	4.70	s
I_2	11° 58′	3.71	w
I_3	15° 54′	2.81	vw
II_0	9° 38′	4.60	vs
II_1	12° 48′	3.48	w

Another possibility for securing new information which may have a bearing on the chain form of rubber and the structure of the unit cell is a comparative study of the x-ray structure of various crystalline derivatives of rubber. Rubber hydrochloride, for instance, gives a crystalline diagram even without stretching, which passes over into an oriented fiber diagram when the material is stretched (23). Rubber hydrobromide shows the same type of structure. Patterns for these materials are reproduced in figures 10 and 11. The fiber identity period in both cases is 9.1 Å. An orthorhombic unit cell with *a* and *c* dimensions equal to twice the lattice spacings of the first two equatorial spots gives in each case fair agreement with the diffraction data and the density, assuming eight repeating groups to be present in the unit cell as for rubber. In the case of the rubber hydrohalides, preparations showing higher orientation have not been obtained. Thus the unit cell is more uncertain than it is for rubber.

Lattice spacings measured for rubber hydrobromide are given in table 4.

The measured density of the unstretched sample (bromine content, 47.8 per cent; theoretical, 53.6 per cent) was 1.51.

Although the addition of hydrohalides causes an appreciable lengthening of the fiber period as compared to rubber, the period is still too short to accommodate a planar zigzag chain with normal valence angles and carbon-carbon distances. The values of the fiber periods are compared in table 5. The angle between the double and single bonds was taken as 125° and that between single bonds as 109° 30′; the bond lengths were taken as 1.54 Å. for single bonds and 1.38 Å. for double bonds (5, 53).

In all these cases a characteristic shortening of the chains exists, so that the question of chain structure is involved in each case for the structure of the unit cell. Current theories of rubber elasticity postulate a statistical shortening of the chain molecules in the unstretched rubber and a straightening of the chains in the stretched condition as the fundamental basis of rubber-like elasticity. Thus, although the chain molecules in the crystallites are somewhat shortened when compared with normal chain forms, nevertheless they would probably have to be regarded as lengthened if compared to a most probable statistical length as determined by the possibilities of rotation about the single bonds.

TABLE 5

Comparison of calculated and measured fiber periods

	FIBER PERIODS CALCULATED FROM PLANAR CHAINS, NORMAL VALENCE ANGLES, AND BOND DISTANCES	FIBER PERIODS FROM X-RAY DIAGRAMS
	Å.	Å.
Rubber	9.3	8.2
Rubber hydrochloride	10.0	9.1
Rubber hydrobromide	10.0	9.1
β-Gutta-percha (20, 30)	10.2	9.54
μ-Polychloroprene (7, 21)	10.2 (*trans*)	9.6

VI. NATURE OF THE CRYSTALLITES IN STRETCHED RUBBER

Hauser and Mark (27) carried out an early investigation which disclosed a number of fundamental facts concerning the nature of the crystalline structure formed in rubber by stretching. As had already been noted by Katz (38), the fiber diagram appeared only if a minimum elongation were exceeded. For evaporated latex sheet, Hauser and Mark found this minimum elongation to be about 80 per cent, agreeing with the value given by Katz. There is every reason to suppose that this minimum elongation depends to some extent on the sample of rubber and on the room temperature. Much higher elongations, 150 to 300 per cent, are usually necessary at temperatures of about 20–25°C. Above the minimum elongation, the intensity of the spots was found to increase approximately linearly with the extension (27, 49), and the amorphous halo to decrease linearly from the start of the stretching. Hock (33) showed that the heat evolved during extension was also proportional to the elongation above a minimum value.

These intensity relations and the conception of a sharp minimum elongation at which the diffraction spots occur for uncured rubber are due to an experimental error. This has been very unfortunte, since the linear relation of the intensity of the spots to the elongation has been difficult to understand and has led to a considerable amount of unsound theorizing.

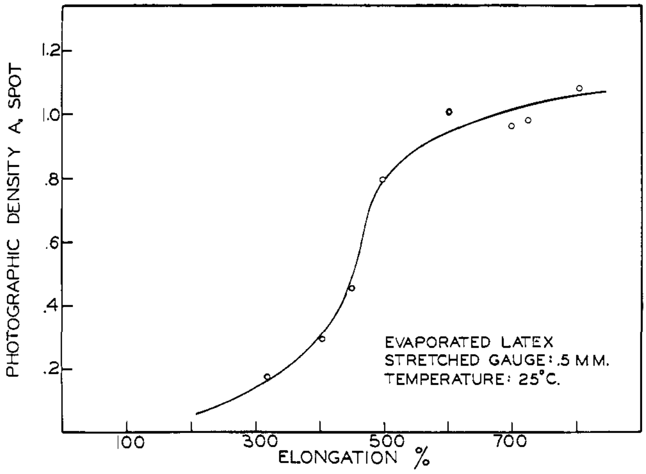


FIG. 12. Intensity of x-ray diffraction and elongation

In the experiments of Hauser and Mark no correction was applied for the diminishing thickness of the rubber as the sample was stretched. If samples of constant final thickness are used, the intensity of the spots is found to be related to the elongation by an S-curve such as is shown in figure 12. This implies that the crystallites begin to form from the start of the stretching and do not suddenly make an appearance. The form of the intensity-elongation curve is thus brought into closer correlation with the stress-strain curve. A study of the shape of the curve under various circumstances for both cured and uncured rubber would be an interesting investigation.

The positions of the interference maxima were found by Hauser and Mark to be independent of the extension within an accuracy of about 0.5 per cent. The "half-value width" of the spots did not change appreciably during stretching. The stretching was therefore considered to be accompanied by an increase in the number of crystallites but not in their size. An improvement in the lattice perfection might also contribute to the greater intensity at higher elongations. Hengstenberg and Mark (31) made precise measurements of the width at half-intensity of the diffraction spots and, using the formula of Laue, arrived at dimensions of width, thickness, and length of 500, 150, and 600 Å., respectively, for the crystallites. No effect of temperature on the size of the crystallites could be measured (51). Diffuseness of the spots due to lattice imperfections would lead to small estimates of size. Most probably, the crystallites show a statistical distribution in size. Beset with uncertainties as calculations of size from the "half-value widths" are, these dimensions are, nevertheless, so much smaller than the molecular chain lengths now believed to exist in rubber, 7000 Å. or more, that the conclusion is fairly certain that a single long-chain molecule may pass through a considerable number of crystallites. For this reason, a secondary or micellar structure, such as was arrived at for natural cellulose fibers (19), has been presumed to exist in rubber (13, 14). It is untenable, however, that any such structure is due to botanical processes, since synthetic materials such as commercial polychloroprene (7, 21) and polyisobutylene (4) show essentially the same type of x-ray diffraction phenomena as natural rubber (see figures 13 and 14). Fisher and Gercke (18) have stated a number of other valid reasons for questioning the occurrence of a micellar structure in rubber. There is the possibility that the ordered regions in stretched rubber represent, in a sense, an unbroken continuity between the liquid structure and the structure of stretched rubber. Thus, comparatively short adjacent portions of the long chain molecules may assume relative orientations such as are now thought to occur for the individual molecules of an ordinary liquid. The formation of an actual space lattice would be favored by the relative immobility of the long chains, which can be thought of as traversing a number of the ordered regions.

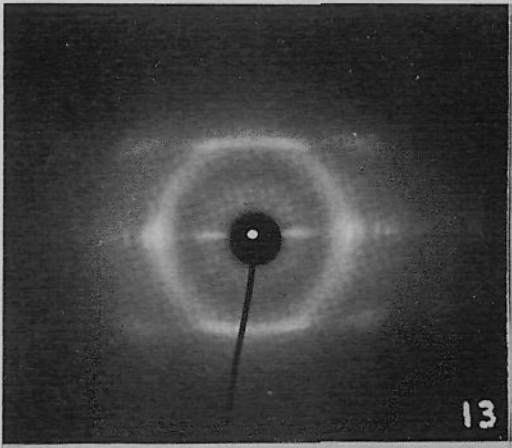
As with frozen rubber, stretched raw rubber exhibits a series of roentgenographically determined melting points depending upon the extent to which crystallization has occurred. Thus, v. Susich (63) plotted a curve of the x-ray fusion point as a function of the elongation for raw rubber. The curve rose from a value of 20°C. at 150 per cent elongation to 90°C. at the highest elongations attainable in the experiments, about 700 per cent. Similarly, Feuchter and Hauser (17), in the course of a comprehensive x-ray study of racked rubber, showed that rubber racked to 600 per cent elongation had a "fusion point" or temperature at which retraction occurred at about 23°C., whereas, when it was racked to 1200 per cent, the fusion point occurred in the range of 35–45°C.

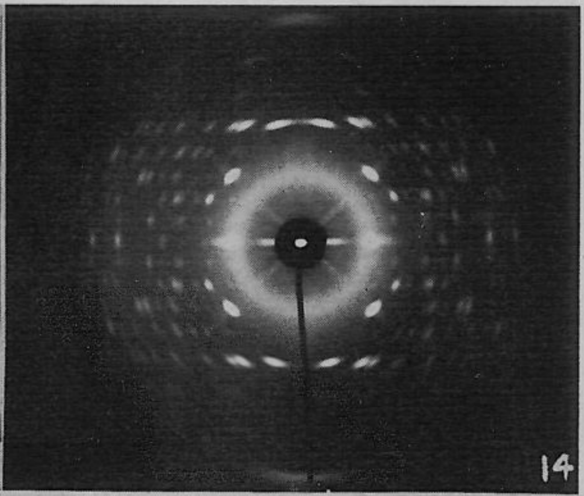
When raw rubber is stretched to intermediate elongations and frozen, crystallization occurs in such a way as to result, not in Debye–Scherrer rings, but in a strong fiber diagram (24). The crystallization proceeds from imperfectly oriented nuclei formed by the stretching. Clark (9) subsequently has published patterns taken under similar circumstances. As the secondary elongation during freezing is only about 5 per cent, this is the maximum elongation which can be thought of as occurring under these circumstances, due to a straightening and alignment of the long chain molecules from the most probable statistical form to the less probable ordered form in the stretched and frozen rubber. Unstretched rubber showing calender effect also gives an oriented diagram, especially when frozen (15, 43). Milling or mastication of crude rubber has the effect of progressively destroying the x-ray interferences upon stretching (27). Deterioration of vulcanized rubber by heating in air also inhibits the appearance of the fiber diagram (35). In the case of milling, it is interesting that the spots apparently diminish in intensity without noticeable increase in breadth, as would be the case if mastication had the effect of diminishing the size of the crystallites. This result falls into line with the views of the crystallite structure previously discussed. Exposure of a stretched piece of rubber to solvent also results in a diminution of intensity of the crystalline interferences (27). If masticated rubber is frozen and then stretched, a mixed Debye–Scherrer and spot pattern is obtained, as is the case for unmasticated, frozen, smoked sheet (28).

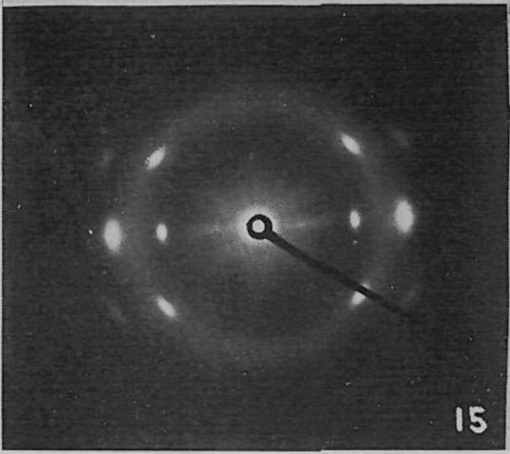
When rubber is vulcanized in a stretched condition at a temperature such that no crystalline structure exists, the resulting structure after vulcanization is also amorphous (29). In the case of cold vulcanization, a permanent fiber structure can be formed by vulcanization under stretch (6).

VII. TIME EFFECTS WITH THE X-RAY DIAGRAM OF STRETCHED RUBBER

Time is a factor in many of the x-ray diffraction phenomena with stretched rubber. The plastic properties are a reflection of internal molecular adjustments which require appreciable time intervals within which to be accomplished. Early in the x-ray work, Hauser, Hünemörder, and Rosbaud (26) found that smoked sheet could be stretched slowly to give an amorphous diagram. More recently, Hintenberger and Neumann (32) have published curves for uncured rubber relating the stress and elongation to the time. They found a well-defined maximum elongation and, in addition, a critical range of loading at comparatively low stresses, within which the rubber test pieces broke, when the elongation was plotted against the stress, the time of loading being constant. X-ray diffraction patterns offered an explanation for these interesting results. For the relatively small stresses below the critical range, the elongation was attained so slowly that an amorphous pattern was secured; for samples stressed above the critical range, a strong fiber diagram resulted. Hence the structures in the stretched samples on either side of the critical range were entirely different. Crystallization is apparently necessary to withstand the higher stresses and to produce the ultimate strength generally associated with rubber.







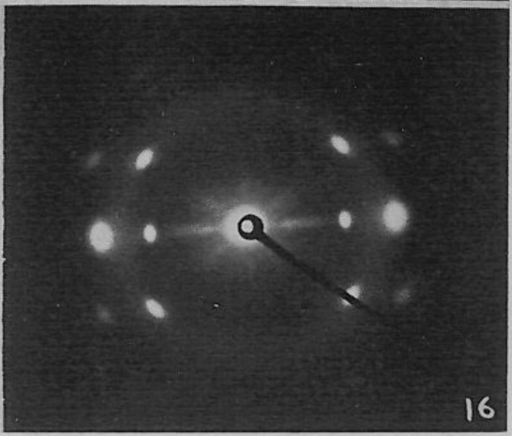


FIG. 13. Stretched polychloroprene (cylindrical camera)
FIG. 14. Pattern for stretched polyisobutylene (cylindrical camera)
FIG. 15. Pattern for a low-modulus gum stock
FIG. 16. Pattern for a high-modulus gum stock

Experiments showing x-ray hysteresis effects for vulcanized rubber were reported by Iguchi and Schoszberger (34). Among other hysteresis effects they found a large effect on the minimum elongation for fibering, depending upon whether the rubber was stretched or relaxed in a continuous or stepwise fashion. Thus, with slow relaxation, crystalline interferences were detected at as low an elongation as 130 per cent, whereas direct stretching required a minimum elongation of about 250 per cent for crystalline interferences.

Katz (37) and also Hauser and Mark (27) found that in some cases crystalline interferences persisted for appreciable periods of time with gradually diminishing intensity after the release of raw rubber which was stretched for a long time. This effect would undoubtedly be quite sensitive to the temperature and can be readily related to the slow approach to a stable equilibrium which rubber shows in practically all its crystallization processes.

A systematic study of the time lag of fibering for a vulcanized rubber compound was carried out by Davy and his associates (1, 45). The rubber underwent a standard stretching cycle and the x-ray beam, by suitable mechanical arrangements, passed through the test piece at definite time intervals after the stretching was completed. Time lags of the order of a second were observed for fibering to occur under the circumstances of the experiments. It would be interesting if such time lags could be related to the extremely variable plastic characteristics of vulcanizates, such as permanent set, creep or drift under load, relaxation of stress at constant elongation, and hysteresis.

Thiessen and Wittstadt (64, 65, 66, 69) observed that the x-ray fiber pattern continued to increase in sharpness and intensity for an appreciable time interval after stretching, an effect which was also investigated by means of double refraction. The change in anisotropy after termination of the stretching was termed "spontaneous orientation." Measurements showed that the orientation tended toward a definite equilibrium depending upon the temperature.

The molecular basis for the numerous hysteresis and drift phenomena with rubber is made evident by the various x-ray phenomena. The continuous slow adjustment of the molecules to new external circumstances of stress and temperature is an outstanding characteristic of the rubber structure.

VIII. THE X-RAY DIAGRAM AND THE PHYSICAL PROPERTIES OF VULCANIZED RUBBER

Since the same x-ray interferences on stretching are invariably obtained for rubber vulcanized under a wide variety of circumstances, it becomes necessary to examine the diagram in various secondary, quantitative ways to look for any information on the molecular structure built up by vulcanization. There are a number of possibilities for such measurements which have scarcely been touched in any serious effort to relate the x-ray diagram to the wide range of properties which can be secured by vulcanization. Katz and Bing (43) carried out an early investigation on the effect of vulcanization on the x-ray diagram, using much higher sulfur contents than is present compounding practice where accelerators are used. Katz and Bing noted that progressive vulcanization tended to necessitate higher elongations for the appearance of the fiber diagram and to render the spots more diffuse. For present-day compounds, the intensity of the pattern also usually decreases somewhat for a technical range of cures as the cure progresses.

The statement is frequently repeated in the literature that the spots appear at an elongation of about 80 per cent for raw rubber and at 250 per cent for cured rubber. As previously stated, such a comparison is entirely a matter of temperature and of the extent of the vulcanization. At temperatures of 20–25°C. higher elongations are usually required for raw rubber. Furthermore, in most cases the comparison is not directly between uncured and cured rubber but between uncured rubber and rubber which has been masticated and subsequently cured. For cured and uncured latex compounds there is comparatively little difference in the intensity of the spots at low elongations such as 300 per cent. In the case of milled compounds, vulcanization does not act to inhibit the appearance of the pattern as is implied by stating that a higher elongation is required. Vulcanization, in this case, may make the pattern possible at room temperature. This state of affairs indicates that the network structure of the vulcanizate assists the crystallization by the same process of molecular immobilization which makes the rubber less sensitive to temperature. This assistance, however, extends only to the point where the rigidity introduced by the network begins to interfere with the movement of the molecules into the crystal lattice. If the network becomes too tight, crystallization is entirely prevented, as in the case of ebonite.

A study of the relation of the intensity of the diffraction spots to the elongation thus affords a possible means for investigating the structure of various vulcanizates. Other indirect experimental methods, such as the effect of temperature on the intensity at different elongations, also are available. The size, shape, and perfection of the crystallites and their orientation may also vary from stock to stock, as is suggested by the different appearance of the spots in the patterns shown in figures 15 and 16, for which the accelerators used were mercaptobenzothiazole and piperidinium pentamethylene dithiocarbamate, respectively. Thus, in spite of the fundamental limitations of the x-ray method and its failure to disclose the length of the chain molecules and dimensions of the network in the vulcanizate, nevertheless a number of indirect approaches remain open for the extension of the work to the problems of vulcanization.

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