COMPARISON BETWEEN THE OBSERVED DENSITY OF CRYSTALLINE RUBBER AND THE DENSITY CALCULATED FROM X-RAY DATA

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ABSTRACT

The density of crystallized rubber may be determined directly or may be computed from the dimensions of the unit cell, which is deduced from X-ray patterns. In early computations, the density obtained was greater than unity, but in recent work computed values have decreased, the lowest quantity reported in the literature being 0.965. In the work described here, there have been determined by direct experiment, the densities of amorphous rubber, of unstretched crystallized rubber, and of rubber crystallized as completely as possible by stretching it. At 25° C, the density of amorphous smoked sheet was found to be 0.906. With purified, amorphous petroleum ether-sol rubber, the values ranged from 0.899 to 0.902 with different preparations of material. At −10° C, the density of crystalline, unstretched smoked sheet varied from 0.950 to 0.952; that of crystalline petroleum ether-sol rubber ranged from 0.948 to 0.951. The density of amorphous smoked sheet at −10° C was 0.932, which was calculated from the value of 0.906 observed at 25° C. That of amorphous petroleum ether-sol at −10° C was 0.928, based on 0.902 observed at 25° C. Smoked sheet stretched almost to the breaking point, and crystallized further at −15° C, had a density of 0.960 at −10° C. Stretching caused an increase, not more than 0.01 greater than that of unstretched crystallized rubber. The increase in stretched rubber is generally believed to be caused by a form of packing in crystallization of a fibrous type. It is reported in the literature that the density becomes constant at 2,000-percent elongation when rubber is racked. Its value, observed presumably at a room temperature, was 0.953. The density at 2,000-percent elongation appears to be that of completely crystallized rubber, and when corrected for the temperature used in any X-ray investigation, is a reasonable guide for deductions about structure.

CONTENTS

I. INTRODUCTION

When unvulcanized rubber is stretched quickly, an orientation of structure occurs parallel to the direction of extension, which is usually regarded as a form of crystallization because of the optical and other phenomena which accompany it. It is also accompanied by a change of volume. When unstretched rubber is subjected to suitable temperatures below about 10° C, it too becomes crystalline. The crystallization of rubber is accompanied by an increase of density, and the simultaneous production of an X-ray diffraction pattern is usually interpreted as evidence that crystallization has occurred. A diffraction pattern of this kind results from the regular repetition, within the crystal structure, of groups of atoms or molecules in a definite spatial arrangement. The smallest group from which the structure can be built up in this way is called the unit cell; and the dimensions can be computed from measurements of the pattern, provided it is possible to determine the crystal form. The pattern of stretched rubber consists of interference spots, and that of frozen rubber consists of rings, but both of their measurements have been shown to indicate the same unit cell. If, in addition, the number of atoms in the unit cell is known, the density of the material can be computed. If the computed density agrees with that found by direct measurement, the fact is a valuable indication of the correctness of the assumed structure on which the calculation of density was based. Accurate knowledge of the density of completely crystallized rubber would therefore serve both as a guide in studies of structure and as a measure of the degree of crystallization of any material under consideration.

In the experimental work described in this paper the rubber was crystallized as completely as possible. Its density was determined by recognized methods and compared with the densities calculated from X-ray measurements.

II. REVIEW OF PREVIOUS WORK

The densities obtained by calculation from X-ray investigations have recently been summarized by Gehman [1].[1] The values vary with the assumptions regarding the unit cell. Until lately they were greater than unity but have tended to decrease in the course of more recent work. The lowest value found in the literature now is 0.965 [2]. The densities measured directly have been less than the computed values, and the differences have been difficult to explain. Perhaps further interpretations of X-ray patterns will reconcile them.

The rhombic cell postulated by Mark and von Susich [3], which undoubtedly had an influence on the configurations assumed in later hypotheses, required that crystallized rubber should have a density of 1.08. According to later measurements of Lotmar and Meyer [4], who assumed that the cell is monoclinic, it should be 1.02. Sauter [5] described another rhombic cell based on the assumed existence of a double reflection. The density computed from this cell is 0.974. Morss [2] attempted to find the true unit cell of rubber, but his conclusions were not entirely satisfactory. The basis of his deductions is a change from 90° to 109.5° of the angle between the two inde-

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[1] Figures in brackets indicate the literature references at the end of this paper.

pendent sets of planes which reflect the two strong equatorial spots. With this modification, the calculated density of the unit cell is 1.00. When Morss applied the angle 109.5° to the measurements of Lotmar and Meyer, the value was 0.965. Misch and van der Wyk [6] have recently obtained photographic evidence of the double reflection which was assumed to exist by Sauter. The cell they postulated resembles that of Morss but contains 16 isoprene units; the calculated density is 0.970.

In the publications of Lotmar and Meyer and of other investigators mentioned above, it is evident that the density 0.965 was accepted as the value to which the unit cell of rubber should conform. This same value was observed by direct measurement by Kirchhof [7], who used smoked sheet which had been stretched to 900-percent elongation and then subjected to a fitting low temperature for further possible crystallization. In the unstretched amorphous state, the density of his material was 0.942. As this value is considerably higher than any of those listed by Wood [8], and as no temperature is mentioned, the determination was probably made at temperatures lower than 25° C or the smoked sheet may have contained abnormally heavy impurities. Lotmar and Meyer, however, obtained the same experimental value as Kirchhof with a crystalline material which was prepared by the evaporation of a solution of rubber in benzene, and subsequently crystallized, but they also did not mention the temperature of measurement. The rubber was held in a well-stretched state at 0° C for 24 hours before the determination.

III. EXPERIMENTAL WORK

1. PREPARATION OF MATERIAL

Because the impurities are disregarded in calculating the density of rubber from X-ray measurements, it was believed desirable to purify rubber for direct determinations. Feuchter [9] has shown that sol fractions of raw rubber are almost free from nitrogen and otherwise quite pure. Accordingly, in the work to be described, unstretched and stretched petroleum ether-sol fractions were used. Smoked sheet and dried latex were also examined for comparison. The rubber used to prepare the petroleum ether-sol had received the following treatment. The latex of *Hevea Brasiliensis*, protected from contamination by bacteria with sodium ethylmercurithiosalicylate, was digested with trypsin to degrade the protein which is in the latex. The water-soluble products of this treatment were largely removed by creaming the rubber three times with a 0.2-percent solution of sodium alginate and withdrawing the layer beneath the creamed material. A small amount of natural antioxidants, equivalent at least to that in raw rubber [10], was added to the rubber dispersion after each separation. After the third separation, the upper layer was centrifuged to remove dirt and was then diluted with distilled water until it contained about 1 percent of rubber. By freezing the diluted dispersion, a loose porous coagulum was formed; and after the ice had melted, residual water-soluble impurities were removed by washing the coagulum with successive portions of distilled water. From the dried product a petroleum ether solution of sol was prepared by a procedure similar to that used earlier. After the sol fraction was separated from the gel,

the petroleum ether was removed by evaporation. Films formed by the evaporation of solutions of rubber in benzene at room temperature were usually free from air bubbles. The residue of sol rubber was dissolved in benzene of reagent quality, and the solution was transferred to an evaporating dish. Transparent, colorless films were formed about 2 mm thick. Rubber which had deposited on the sides of the dish was cut away. The dish was placed in distilled water, and when the deposit on the bottom could readily be detached, samples weighing between 1 and 1.5 g were cut to a suitable shape under water. The samples were dried to constant weight at 100° C in a stream of nitrogen.

With the purpose of increasing mobility during crystallization at a suitable low temperature, a plastic rubber was prepared by disaggregating with piperidine a sol fraction dissolved in benzene. The piperidine was subsequently extracted from the product with successive portions of acetone, at room temperature. After the disaggregated rubber had been chilled at −10° C for 30 minutes, it could be elongated to at least twice its original length.

2. METHODS OF CRYSTALLIZATION

The marked discrepancy between the calculated and experimentally determined values persisted in spite of the precise X-ray measurements of Lotmar and Meyer, and may well cast doubt on the experimental value if the assumptions leading to the calculation of the axes of the unit cell are accepted. Consequently it seemed possible that by some special experimental procedures rubber could be crystallized to a higher degree and thus have a higher determined density than any reported in the literature. Some of the procedures were based in part on the conception of the rubber molecule as a long chain with angular configuration. The chains, if they are assumed to exist as a tangled, interlacing mass and to possess secondary valence forces, can perhaps be oriented with difficulty. It was thought that very slow elongation might cause more perfect alinement because, under this condition, the forces of attraction and repulsion along the sides of the molecule would be given greater freedom. Strips about 25 mm wide and 1 mm thick were stretched at various slow rates, at room temperature and also at −10° C and at −20° C, immediately after they had become chilled. To determine the effect of rapid stretching, other strips were extended suddenly at these temperatures. According to another concept of rubber structure, needle-shaped molecules may exist in groups of micelles. During disaggregation, a separation of the molecules might be expected to occur, accompanied by increased mobility. Strips of disaggregated rubber were chilled to −10° C and to −20° C to decrease mobility and minimize any disorganization caused by the heat of stretching, and then stretched quickly to maximum elongation. Others were stretched in successive small steps to maximum elongation during 20 minutes, before crystallization became pronounced. None of the various special methods described above had any effect. The samples with which the results in table 1 were obtained had been subjected to temperatures of about −15° C for different periods, none longer than 30 days, before the determinations were made.

3. METHODS OF DETERMINING DENSITY

The densities were determined by the hydrostatic method in an immersion mixture consisting of equal parts by weight of acetone and water. They were also determined by adjusting the amounts of acetone and water until the mixture had the same density as the specimen, and the density of the mixture was determined. The hydrostatic method involved the use of an analytical balance. A strip of rubber about 70 mm long, which had been cut with chilled shears, was held on a stiff platinum wire, the end of which was bent to form a rigid support. The immersion mixture was contained in a Dewar flask, and its density was found with a precision type of Westphal balance, suitably corrected. The determinations were made usually to about one-thousandth of a unit. If greater precision was desired, the effect of the cold immersion mixture on the arm of the balance was noted, a small amount of a suitable wetting agent was added to minimize surface drag on the wire, and the observations were made as rapidly as possible. Since some forms of crystalline rubber have sometimes been observed to melt below 0° C, a temperature of −10° C was used in this work for density determinations of crystalline material, to avoid melting and also to suppress the tendency of the rubber to swell in the acetone-water mixture. With amorphous rubber, a temperature of 25° C was used, and the sample was attached to a sinker in distilled water as the immersion liquid. Air which adhered to the surface of a specimen immersed in water, or in a mixture of water and acetone, was removed. After a determination of density, the sample was dried in air and placed in dimethyl phthalate, which has approximately the refractive index of rubber. Air in the sample was readily observed, and when necessary the amount of it was estimated.[2] The highest correction applied to the density because of included air was 0.001.

IV. RESULTS FROM DENSITY DETERMINATIONS

Typical values of the density of amorphous rubber and of crystalline rubber at −10° are given in table 1. With crystalline unstretched smoked sheet, the results vary between 0.950 and 0.952; and with crystalline unstretched petroleum ether-sol, they range from 0.948 to 0.951. The results which show the effect of stretching upon smoked sheet represent successive elongations of 100 percent. The increase in density is slight, not more than 0.01. The last quantity, 0.960, was obtained with a sample extended beyond 1,000 percent, almost to the breaking point. Higher densities than 0.960 were possible only by racking the rubber. The density of amorphous smoked sheet at −10° C is calculated by the formula of Bekkedahl [11], using the value 0.906, which was observed at 25° C; that of amorphous sol rubber from 0.902, the highest density observed with this material at 25° C. This value is lower than any of the values listed by Wood [8]. However, in addition to this quantity of 0.902, other densities were observed ranging as low as 0.899 with different lots of sol rubber. Repeated observations with any single preparation agreed to the third decimal place. In spite of attempts to find a source of error, the differences in different lots of sol rubber persisted.

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[2] By C. P. Saylor, of this Bureau.

TABLE 1.—*Densities of amorphous rubber and of crystalline rubber at* −*10° C*

[The densities of amorphous rubber at −10° C were calculated from values obtained at 25° C.]

Petroleum ether-sol		Smoked sheet			
Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Crystalline stretched (−10° C)	
				Density	Elongation
0.928	0.946	0.932	0.951	0.954	% 100
	.945		.952	.956	200
	.944		.951	.956	300
	.943		.950	.956	400
				.956	500
				.957	600
				.957	700
				.957	800
				.958	900
				.958	1,000
				.960	>1,000

In addition to the values listed, some determinations were made with miscellaneous samples prepared in various ways. When dried strips, prepared by the evaporation of dialyzed latex, were extended to various amounts between 100-percent and 1,000-percent elongations and subjected to a temperature of −15° C while stretched, their densities were the same as those observed when smoked sheet was elongated (table 1), and stretching caused an increase of not more than 0.01. The density at −10° C of disaggregated rubber after chilling was 0.951, which is in the range observed with sol rubber. That of smoked sheet which had been stored without pressure at 0° C for approximately 5 years was 0.957 at −10° C. To determine the effect of pressure in the absence of orientation, sol rubber was placed in a square, confined space with sides about 1 cm², and squeezed by a piston under a pressure of about 1,000 atmospheres, at room temperature for 8 hours. While the pressure was maintained, the rubber was crystallized during 12 hours, at −10° C. Its density was 0.951. The same value obtained without pressure is listed in the table of results. Pressure from all sides of the confining space did not in this case increase the density.

The rate at which rubber crystallizes at −20° C was observed with unstretched specimens cut from adjacent areas of a smoked sheet. The initial density, 0.929, of amorphous rubber at −20° C was calculated from Wood's publication [8] on physical constants of rubber, because crystallization occurred during attempts to determine it. The densities at successive intervals were as follows: after 3 hours, 0.935; 5 hours, 0.950; 24 hours, 0.955; 1 week, 0.955. When these values were plotted, a curve was obtained which was similar in shape to that reported by Bekkedahl [11] for the rate observed at 0° C. At −20° C the transition was faster.

In earlier work [12] stretched rubber, maintained in an extended state, was observed to increase in length when subjected to suitable low temperatures. According to the explanation which was suggested, stretching establishes a crystal lattice with crystals oriented parallel to the direction of elongation, and when more molecules enter it,

they too assume the parallel direction. The rubber elongates because of the shape of the molecule until molecular movement is inhibited by random crystallization of the residual rubber. To determine whether a marked change of density occurs during the secondary extension, the following procedure was used. A strip of uniform width and thickness from dried latex was extended, fastened at both ends and at the middle, forming two sections, and immediately exposed to a temperature of −20° C. When the extension had definitely commenced, a specimen was cut from one section and its density determined as quickly as possible by the hydrostatic method to a ten-thousandth of a unit. After the extension had become completely established, about 20 minutes later, a specimen from the second section was examined. The amount of elongation was the difference between the length of the specimen after its density had been determined, and the length after the specimen had subsequently been allowed to retract at room temperature for 24 hours. With one sample the density before secondary extension was 0.9449 and the elongation 380 percent; at maximum secondary extension it was 0.9456 at an elongation of 440 percent. With another sample the density before secondary extension was 0.9386 at 130-percent elongation, and 0.9391 afterward at 195-percent elongation. The increase of density with the first sample, 0.0007, during a secondary extension of 60 percent, amounts to 0.0071, when the increase is based on 1,000-percent elongation less the original elongation before secondary extension took place. The increase of density of the second sample, 0.0005, during a secondary extension of 65 percent, becomes 0.0067 on the same basis. These increases agree closely with the results obtained with smoked sheet, based on 1,000-percent elongation, in table 1. There the minimum increase is 0.006 and the maximum 0.008.

V. DISCUSSION OF RESULTS

The change of volume which takes place during the elongation of rubber appears to be the result of the formation of crystals of the same type as those formed when rubber is cooled. The fact that calculations of the dimensions of unit cells from X-ray data lead to the same result in the two cases suggests this. The increase of density during elongation is usually ascribed to a form of packing in crystallization of an oriented fibrous type, which takes place. The increase continues during racking, but becomes constant at 2,000-percent elongation, at which Feuchter [13] found a density of 0.953, apparently at some room temperature. If a probable temperature of 20° C is assumed, at −10° C it would be 0.970.

If density is to be used to aid in the interpretation of X-ray diffraction patterns, the effect of temperature should not be disregarded, because rubber has a large coefficient of expansion.

The density of rubber, completely crystallized when stretched, appears to be the limiting density reported by Feuchter, for the following reason. In X-ray diagrams of stretched rubber, the position of the diffraction spots is independent of the elongation but the spots become more intense as the elongation increases, that is, with the increase of packing. This suggests that the maximum effect represents an orientation that is substantially complete. Recently, Field [14] developed a method of measuring the amount of crystallinity in stretched rubber. At high elongations the maximum amount found was about 80 percent of the total. For total crystallinity a density

of 0.965 was deduced. Treloar [15] estimates that the increase of density during crystallization is not less than 3.75 percent. The reports of several observers, who have examined types of sol and gel rubber of varying degrees of aggregation by X-ray technique, indicate that crystallinity is developed and retained most readily in the stretched gel fraction. Consequently, when rubber is stretched there appears to be a relation between the degree of polymerization and the amount of crystalline material formed.

The range of densities, 0.899 to 0.902, observed with amorphous petroleum ether-sol rubber in this work is much less than the differences shown by results reported in the literature and summarized by Wood [8]. The following values are quoted from the summary. With unpurified rubber at 25° C, Bunschoten found a density of 0.905; Whitby, 0.906; McCallum and Whitby, 0.918; and Feuchter, 0.928. With purified rubber at the same temperature, Weber found 0.905; McPherson, 0.906; McCallum and Whitby, 0.9207; and Bondy (Staudinger), 0.9208. Recently Kemp [16] reported densities of petroleum ether-sol rubber, determined at 20° C, which varied from 0.905 to 0.910. At 25° C, this corresponds to a density range from 0.902 to 0.905. With impure and with purified material, the lack of agreement is significant, and the densities of sol rubber, 0.899 to 0.902, agree with none of the values quoted. Perhaps the low values obtained in this work represent the densities of depolymerized material. By this term is meant a disruption of long-chain molecules into short ones characterized by lowered viscosity and molecular weight, and decreased tensile strength. In long-chain molecules of high molecular weight, for example 100,000, forces of attraction and repulsion at the ends must be negligible. The molecule substantially is one consisting of two sides. If the long molecule is broken into many short ones, it is possible that disruption may continue until the ends of short molecules cause significant attraction and repulsion. An increase of volume would result. Unfortunately, nothing is known about the degree of depolymerization which is necessary to cause a change of volume. Furthermore, any proposed explanation for the ranges of density observed must be viewed with skepticism, because no structure which has been proposed for rubber has received complete acceptance.

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