

RUBBERS AND THEIR CHARACTERISTICS: REAL AND IDEAL*

By DR. L. R. G. TRELOAR

British Rubber Producers' Research Association

Chemical Structure of Rubbers

NATURAL rubber, extracted from latex by coagulation with acid, and afterwards washed and rolled, appears on the market as crepe or smoked sheet. Raw rubber, as these materials are called, is essentially a hydrocarbon (C₅H₈)_n having the chemical structure shown in Fig. 1. It is a polymer of isoprene, the isoprene units being joined together in the form of a long chain. The actual length of the molecular chain, or *molecular weight*, of rubber has been the subject of much discussion, estimates obtained by different methods having ranged from about 1,000 to about 500,000; and it is only within the last few years that the question has been settled. The reliable measurements of Dr. G. Gee show that the mean molecular weight of a typical raw rubber is about 350,000, corresponding to a chain of about five thousand isoprene units.

This long-chain molecular structure accounts for the very high viscosity of rubber solutions in ordinary solvents like benzene. We imagine that the resistance to flow is due largely to the mutual interferences and loose entanglements between these very long molecules. However, raw rubber is ultimately completely soluble, and we conclude, therefore, that the molecules are not in any way chemically joined together.

It is otherwise with vulcanized rubber, which swells considerably in solvents (to five or ten times its original size), as if it were trying to dissolve, and yet does not go into solution at all. In this case it is reasonable to suppose that the vulcanization (that is, chemical combination with sulphur) has led to a cross-linking of the molecules (see below).

Fig. 1 is intended to show the diversity of chemical composition of materials which, under certain conditions, show rubber-like elasticity. Whereas most practical rubbers are built up on a chain of carbon atoms, this is by no means an essential feature, as the examples of gelatin and elastic sulphur show. The important and invariable feature of all rubbers is the pattern of their molecular structure; there is no highly elastic material, so far as I am aware, which is not built up of very long chain-like molecules.

Origin of the Elasticity.

Until about twelve years ago, none of the theories of the elasticity of rubber which had been proposed could be regarded as even approximately satisfactory. Attempts to interpret long-range elasticity on the basis of interatomic forces were manifestly inadequate, and it was not until Meyer, v. Susich and Valko introduced the conception of a *dynamic*, in contrast to a *static*, basis for the phenomenon that the mystery was solved. The theory developed rapidly through the work of Guth and Mark and of Kuhn, and is now generally accepted as representing the correct method of approach.

To understand the kinetic point of view we must first examine the form of a long-chain molecule, considered as an isolated unit. For this purpose it is usual to consider the simplest possible chain structure, namely, the paraffin molecule. The assumption is

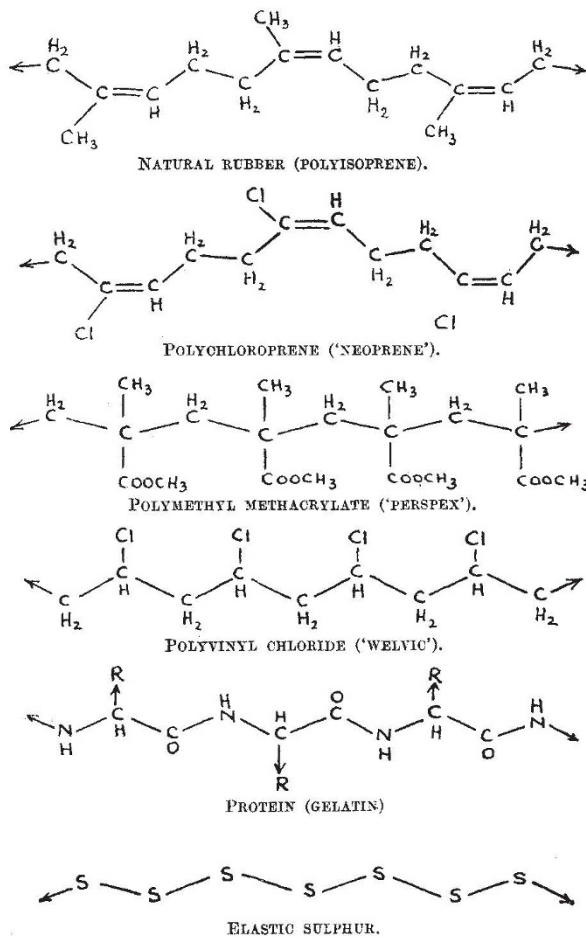


Fig. 1.

made that the carbon atoms of the chain are in a state of continual thermal vibration, so that they may take up any relative positions consistent with the maintenance of a fixed bond-length and a fixed angle between bonds (109½°). According to this assumption, each C—C bond may be regarded as rotating freely about the preceding bond as axis. There is chemical evidence that such rotation does take place. In consequence of this random rotation about bonds, the chain will not be a uniform zigzag in one plane, as in Fig 2a, but will assume a randomly kinked form in three dimensions, as indicated in Fig. 2b. The distance between the ends of the chain in this form is likely to be very much less than the outstretched length of the molecule in Fig. 2a, and the statistical treatment of the problem enables the probability of any given end-to-end distance to be calculated. The function representing this probability turns out to be the ordinary Gaussian error function,

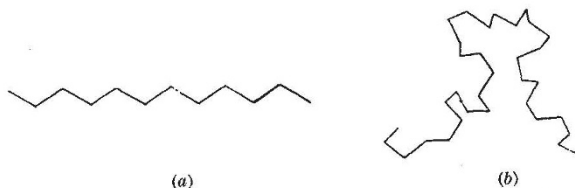


Fig. 2. PARAFFIN CHAINS: (a) PLANAR ZIG-ZAG; (b) RANDOMLY KINKED.

* Royal Institution discourse delivered on December 15.

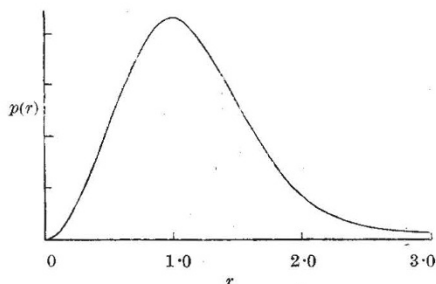


Fig. 3. FUNCTION REPRESENTING THE PROBABILITY $p(r)$ THAT A MOLECULE HAS THE LENGTH r .

which is represented in Fig. 3. The normal state of the free molecule may be identified with the maximum of this curve; that is, it is the most probable state, and the corresponding length is found to be proportional to the square root of the number of 'links' in the chain.

We see, then, that if the molecule is forcibly extended, and then released, the random thermal motion will rapidly restore it to a length not very different from the statistically most probable length. The molecule, therefore, exhibits elasticity. Moreover, its elastic extensibility is proportional to the square root of the number of chain links, or the molecular weight. This theory, therefore, explains in a natural manner why long-range extensibility is found only in association with chain-like molecules of very great length.

The thermodynamic development of the kinetic theory leads to some rather striking conclusions. Two of the more important of these are:

- (a) In rubber held at constant extension, the tension is proportional to the absolute temperature.
- (b) The extension of rubber takes place without change in its internal energy; hence there is an evolution of heat equal to the work done on the rubber by the stretching force.

In these two respects the behaviour of rubbers is closely analogous to that of a gas. The agreement with experiment which is found provides very strong evidence in favour of the theory.

The Ideal Rubber

Thus far our attention has been focused on the individual molecule. We have yet to consider in more detail how the elastic properties of the molecule are to be conveyed to the material in bulk. When we consider this problem, we see that in order to be able to take up a variety of statistical forms in the way required by the theory, the molecular chains must have a freedom of movement comparable with that in a liquid. On the other hand, for the rubber to maintain a permanent shape, and to resist applied stresses, the molecules must somehow be fixed in their average positions relatively to one another. To meet these two rather contradictory requirements it is necessary to think of the molecules as linked together by a relatively small number of unbreakable bonds. These will be present in sufficient numbers to produce a complete three-dimensional network throughout the material, but owing to the great length of the chains they need not seriously impede the freedom of motion of the segments of molecules between such points of junction.

We are thus led to postulate three necessary conditions for the occurrence of rubber-like elasticity, namely:

- (1) The presence of long-chain molecules, with freely rotating links.
- (2) Weak secondary forces around these molecules.
- (3) A few points of cross-linkage, resulting in a loose 3-dimensional network.

The ideal rubber may be thought of as a permanent network of long-chain molecules held together by unbreakable bonds, but otherwise completely free to move. The stress-strain properties of such an ideal network have been worked out by a number of authors. The most satisfactory development in this direction is due to Wall (1942), who obtained the following equations for the case of a simple elongation (or uni-directional compression) and simple shear respectively:

For elongation,

$$F_{\alpha} = NkT \left(\alpha - \frac{1}{\alpha^2} \right),$$

where F_{α} is stretching force, referred to original section of 1 cm.², N is number of 'molecules', a 'molecule' being the length of chain between its points of junction to the network, k is Boltzmann's constant, T is absolute temperature, and α is the ratio of stretched to unstretched length.

For simple shear,

$$F_{\sigma} = NkT\sigma,$$

where F_{σ} is shear stress and σ is amount of shear.

There are a number of particularly interesting features of these equations. First, the stress-strain curve for elongation is non-linear, that is, Hooke's Law does not apply, while for shear the relation is linear. Secondly, the only molecular property which enters into these equations is N , the number of chain elements in the network. This quantity is simply related to the 'molecular weight' of the chain. The precise constitution of the molecule or the number of freely rotating links which it contains is of no significance in this connexion. The third point, which is related to this, is that one physical constant only is sufficient to define the elastic properties of a highly elastic material.

I have extended the elastic network theory to the case of a deformation of any type, and shown experi-

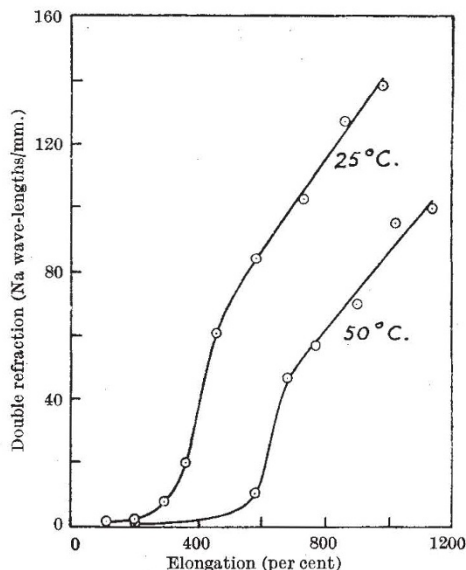


Fig. 4. DOUBLE REFRACTION IN RAW RUBBER. EACH POINT REFERS TO A FRESH PIECE OF SHEET HELD AT THE APPROPRIATE EXTENSION FOR ONE HOUR.

mentally that the resultant equations give a reasonably satisfactory account of the properties of well-vulcanized rubber under a number of different types of deformation, except under very high strains, when the underlying assumptions of the theory are no longer applicable.

Application to Real Materials

Having now defined the conditions under which rubber-like behaviour is to be expected, let us inquire to what extent real materials satisfy these conditions, and the way in which the non-fulfilment of these conditions leads to departures from the simple behaviour of the ideal rubber.

The first point of difference is that in practice rubber-like properties appear only within a certain range of temperature. At low temperatures rubbers are transformed to a glass-hard condition. Below the transition temperature the molecular chains become immobile, the thermal energy no longer being sufficient to overcome the secondary forces between the molecules. For a material like natural rubber, these secondary forces are relatively weak, and the transition temperature is very low ($-70^{\circ}\text{C}.$). If the intermolecular forces are comparatively strong, the transition temperature is very much higher. This is exemplified by polymethylmethacrylate (Fig. 1), which is a glass at normal temperatures (being extensively used for its non-splintering property), but becomes highly elastic above about $70^{\circ}\text{C}.$

Rubber-like properties may also be lost at high temperatures, where, in the case of polymers which are not cross-linked, the molecules become sufficiently mobile to slide bodily past one another, the rubber thus becoming a viscous liquid. The longer the molecules, the higher the temperature at which this effect becomes noticeable.

This plastic property of rubber and the 'thermo-plastics' is made use of in the processes of moulding, extrusion, etc. In the case of rubber the final form is 'fixed' by vulcanization—that is, combination with sulphur—which leads to a chemical cross-linking of the molecules.

Crystallization

So far I have omitted one very important phenomenon which profoundly affects the mechanical behaviour of rubber, namely, crystallization. If raw rubber is held at temperatures below $0^{\circ}\text{C}.$ for several days, it becomes comparatively hard and inelastic, and at the same time loses its transparency. This state is not to be confused with the glassy state, which occurs on quickly cooling to very much lower temperatures. The X-ray diffraction pattern of normal 'amorphous' rubber is like that of a liquid, there being only a single broad halo present. The same pattern is given in the glass-hard state. But the slowly frozen rubber shows a number of well-defined rings, which are to be interpreted as due to the presence of crystallites oriented at random, as in a powder.

Owing to the enormous length of the molecules, there are significant differences between the process of crystallization in rubber and in an ordinary low-molecular liquid. The crystallites are separated by regions of 'amorphous' or disordered molecules (crystallization is never complete), and, furthermore, a single molecule may pass alternately through several crystalline and amorphous regions. Thus the crystallites are bound together by amorphous rubber. This

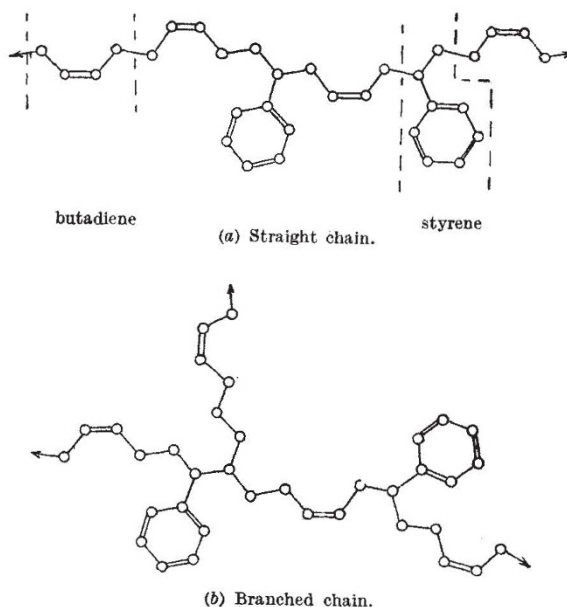


Fig. 5. POSSIBLE CHAIN FORMS FOR SYNTHETIC RUBBER GR-S (BUTADIENE-STYRENE POLYMER)

intimate binding of amorphous and crystalline components leads to a certain indefiniteness in the melting point of the crystalline phase, but at the same time imparts a degree of flexibility or toughness which is normally absent from crystalline bodies. The peculiar advantages of this type of molecular structure are made use of in polyethylene, which is chemically the same as paraffin wax, but has a much higher molecular weight. It is flexible, yet sufficiently hard for use as a cable-insulating material, and since the crystals hold the structure together vulcanization is unnecessary. The exceptionally valuable dielectric properties of the pure hydrocarbon are thus unimpaired.

Crystallization occurs not only in unstretched rubber at low temperatures, but also in stretched rubber at ordinary temperatures. By stretching, the molecules are brought into an approximately parallel arrangement, which greatly facilitates the crystallization process.

In stretched crystalline rubber the crystals all have one axis pointing in a fixed direction. Viewed by X-rays, this kind of arrangement gives rise to a series of spots arranged in a characteristic pattern. This pattern bears a rather strong resemblance to the X-ray pattern of natural fibres (cotton, wool, etc.), and in fact, stretched crystalline rubber behaves mechanically like a fibrous material, as Hock showed in 1924. If stretched crystalline rubber is frozen in liquid air and hammered, it splits along the fibre axis, just like a piece of wood. Also, it is very easily torn along the direction of the grain, but is, of course, exceedingly tough in other directions.

The rubber crystal is birefringent, hence stretched rubber is highly doubly refracting. If a piece of vulcanized rubber is stretched between crossed 'Polaroid' plates, a succession of brilliant interference colours is developed as the extension increases; on retraction, the effect disappears. If the same is done with unvulcanized rubber, the effect does not disappear entirely on removal of the tension; in this case the crystals are more permanent. The

method may be employed for the quantitative study of crystallization in stretched rubber. Fig. 4 shows the birefringence of raw rubber as a function of the elongation.

The Synthetic Rubber GR-S

Before concluding, I should like to devote a few words to the consideration of the general purpose synthetic rubber GR-S now being produced in considerable quantities. This rubber, like the German 'Buna', is formed by polymerizing together butadiene and styrene. The chains are thus lacking in regularity (Fig. 5), since these two components occur in a random order, with the result that crystallization is not possible. This probably accounts for the much lower tensile strength of GR-S vulcanizates which do not contain a reinforcing agent like carbon black, compared with similar natural rubber vulcanizates. Moreover, there would appear to be a possibility of the formation of branched chains (Fig. 5*b*) leading to a cross-linked structure. It is suggested that this effect may account not only for the comparative difficulty encountered in milling it to a suitable softness, but also for its most unfortunate lack of self-adhesion. Self-adhesion involves a mutual diffusion at the surface of contact; any branching or cross-linking of the chains will considerably reduce such diffusion.

DIAGNOSIS OF MINERAL DEFICIENCIES IN CROP PLANTS*

By PROF. T. WALLACE

Long Ashton Research Station, Bristol

LIEBIG, in enunciating his mineral theory of the nutrition of crops in 1840, advanced the view that simple plant analysis would suffice to provide the data to determine the mineral requirements of crop plants and the amounts of mineral nutrients necessary to add to the soil to make good shortages due to removals by crops.

The field experiments of Lawes and Gilbert soon showed this conception to be erroneous and resulted in attention being focused on field trials and soil analysis as means of solving problems of crop nutrition, including deficiencies of mineral elements. From that time until 1920, these remained practically the only two methods in general use for determining deficiencies of mineral nutrients and the fertilizer needs of crops, and they still continue to play important parts in the solution of these problems.

Since 1920, however, other methods for diagnosing the mineral status of crop plants have been developed, based primarily on the plants themselves. In attacking problems in the field these methods are given complementary roles, and field trials and soil analysis are also included, with the result that problems are attacked from many angles and a choice of methods is available to suit the varied conditions which occur.

The new methods include visual diagnosis, foliage spraying, injection of leaves and stems, and chemical analysis of leaf laminae and petioles and of stems.

In practice it has been found that none of the methods used alone will provide a complete solution of deficiency problems in all circumstances, but when

used in complementary roles and with varied emphasis to suit different conditions, they have proved effective in solving very diverse and difficult problems.

Visual Symptoms of Mineral Deficiencies*

The visual symptoms which result from mineral deficiencies in crop plants have proved a valuable aid in diagnosis and form the basis of the visual method discussed later. In view of the importance of this method to technical agriculturists, it was considered worth while to devote one lecture entirely to the subject of deficiency symptoms.

Although the symptoms produced are very varied they allow of some classification and grouping. Thus deficiencies of nitrogen, phosphorus, potassium and magnesium always affect older tissues first, and the visual signs progress systematically from the older to the younger parts of the plants, whereas the deficiency effects of calcium, iron and boron invariably appear first in meristematic tissues and often result in the death of growing points.

In field crops in Great Britain, deficiencies of all the essential elements, with the exception of sulphur, copper, zinc and molybdenum, have been recorded and frequently occur, and it is thus of interest to summarize some of the main features of the deficiency effects which have been observed.

The effects produced by nitrogen deficiency are very consistent over a wide range of plants. Growth is greatly reduced, stems are upright and thin, and lateral shoots are few, leaves are small and usually pale green in colour, flowering and fruiting are much reduced, and autumn tints of leaves, stems and fruits are usually brilliant, consisting of yellow, orange, red and purple colours. Defoliation is premature.

Phosphorus deficiency produces many effects similar to those resulting from nitrogen deficiency, but leaf symptoms are more variable. They may take the form of high colorations as for nitrogen deficiency; but more often the tints are dull shades of purple, or tints may be absent altogether, the leaves remaining a dull, lustreless, olive green, or the margins may become 'scorched'.

Potassium-deficient plants are generally squat in habit because of short stem internodes and, unlike deficiencies of nitrogen and phosphorus, lateral shoots may be abundant while shoots may die back. Marginal leaf scorch is a very common symptom, but leaves may also show tip scorch, chlorosis, spotting and backward or forward curling of the laminae. Bright tints are often lacking, though not invariably so.

Calcium deficiency results in the death of the growing points of shoots, which condition may lead to the development of adventitious laterals, and in the distortion, wilting and scorching of leaf margins, collapse of petioles and the death of flowers. Root growth is much restricted and tuber formation seriously affected.

Magnesium deficiency is remarkable for the diversity of leaf effects produced. These include chlorosis, brilliant tinting with well-defined colour patterns, interveinal necrosis (both central and marginal) and spotting. The effects produced are often highly spectacular and ornamental. Defoliation is generally serious and may follow very quickly after the appearance of leaf symptoms. Deficiency effects usually develop at a relatively late stage of growth.

* Summary of two lectures delivered at the Royal Institution on January 30 and February 6.

* For a full account and for illustrations of visual symptoms, see "The Diagnosis of Mineral Deficiencies in Plants by Visual Symptoms" (with 1944 Supplement) by T. Wallace. (H.M. Stationery Office.) 15s.