THE STATE OF AGGREGATION OF RUBBER AND OF SUBSTANCES WITH RUBBER-LIKE EXTENSIBILITY

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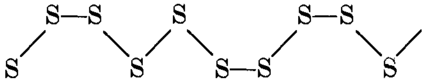
Among the transition states between the classical three states of aggregation it is now possible, on the basis of recent work, to define and understand the characteristics of a certain state,—the state of aggregation of rubber and of other substances with similar mechanical properties.

I. OCCURRENCE OF THE RUBBER-LIKE STATE OF AGGREGATION ("RUBBER-LIKE STATE")

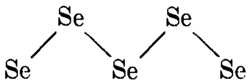
The number of substances that can occur in a rubber-like state is not very large, although considerably greater than is generally realized. The following list shows that this state is not associated with particular elements or chemical groups, and that it is found (*A*) in polymers of chemically regular or uniform structure, and (*B*) in irregularly constituted substances with a chain structure.

Class A: Substances in which atoms or atom-groups of the same kind are linked together in chain-like form:—

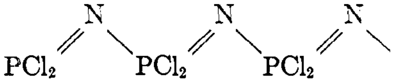
Elastic sulfur (18, 30):



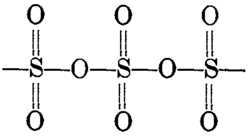
Elastic selenium (23):



Phosphonitrilic chloride (20, 25, 28):

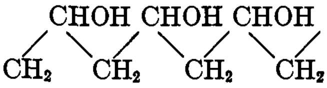


Polymeric sulfur trioxide (3):

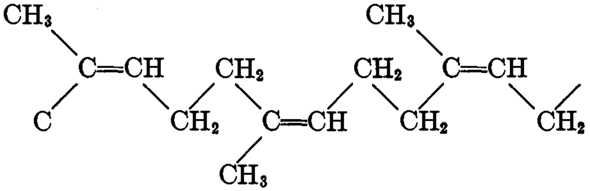


$$-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-$$

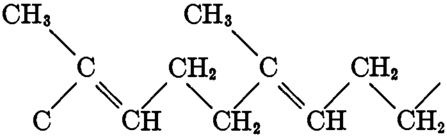
Polyvinyl alcohol (5):



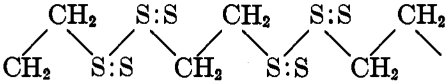
Rubber:



Guttapercha (above 60°C.):



Polyethylene tetrasulfide (24a):



Class B: Chain polymers of irregular constitution:—rubber of medium degree of vulcanization; synthetic rubber, e.g., Buna; polyvinyl acetate (above 60°C.); animal elastic fibers, e.g., in the *Ligamentum nuchae* of the ox; tendinous fibers and elastoidin fibers contracted by heat; muscle fibrils in the uncontracted state.

II. ATOMIC ARRANGEMENT

As x-ray photographs show, no crystalline lattice-like arrangement exists in the rubber-like state in an unstretched object. The x-ray diagram shows only one or more indistinct rings. An interpretation of such "amorphous diagrams," so far as this is possible, has recently been tried by Warren (27) with amorphous rubber. The distribution of intensity is compatible with the assumption that at a distance of 1.5 Å. from each CH_2

group there are two other CH_2 groups and, further, four groups at a distance of between 4 and 5 Å. It must therefore be assumed that the chains do not lie stretched out and side by side, but that, owing to the free rotation around the single bonds, they take up other possible forms.

During the passive stretching of substances belonging to class A the long, primary-valence chains arrange themselves along the fiber direction and "snap" into lattice-like arrangements (9, 12), whereby heat of the nature of heat of crystallization is liberated (6).

The crystalline structures formed during stretching no longer show extensibility; the atoms in these structures are in the same state as in other crystalline bodies. Crystallization thus occurs as a phenomenon accompanying stretching, but has nothing to do with the essential nature of the rubber-like state. This follows also from the behavior of substances in class B. With these the occurrence of crystallization is either entirely absent or incomplete. With vulcanized rubber, for instance, it decreases with increase in the amount of combined sulfur, and hence in the irregularity of the structure, until at about 8 per cent sulfur it disappears entirely, while the characteristic elasticity is not impaired. With polyvinyl acetate there is only one "point" on the equator, according to the observations of Katz (10); this shows that the chains have a parallel orientation but not a lattice-like arrangement.

III. THERMODYNAMIC CONSIDERATION OF RUBBER-LIKE BODIES (1, 8a, 16, 24, 33)

If a stretched rubber-like body is in equilibrium with the deforming tensile force, the equations of thermodynamics can be applied to it. A simplification arises from the fact that the changes in volume during stretching and contraction can be neglected and therefore $A = F$ and $E = H$.

By determining the manner in which the force exerted by a stretched rubber-like body depends on the temperature, it is possible to separate the free energy of contraction A into its components,—the energy component E and the entropy component TS,—and thereby to arrive at certain conclusions regarding the molecular process occurring during stretching and hence the molecular structure of the rubber-like body itself.

If we denote by K the force exerted and by l the length of the stretched rubber-like body, then we have:

$$K = \left(\frac{\partial E}{\partial l}\right)_T + T\left(\frac{\partial K}{\partial T}\right)_l$$

$$\left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T$$

Within a small temperature range K can be expressed as a linear function of T (i.e., the curve can be replaced by its tangent):

$$K = a + bT$$

and thus

$$a = \left(\frac{\partial E}{\partial l}\right)_T \quad \text{and} \quad b = \left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T$$

From this the following deductions can be made:

If the force (K) is independent of temperature, then S remains constant during isothermal contraction or stretching; if the force increases with the temperature, S increases during contraction and, if K decreases, S becomes smaller during contraction.

If, within a given range, K varies in proportion to the absolute temperature, i.e., $K = bT$, then $\left(\frac{dE}{dl}\right)_T = 0$; hence an isothermal contraction or stretching is not accompanied by any change in E. If K is smaller than bT, then $\left(\frac{dE}{dl}\right)_T < 0$, which means that E increases during isothermal contraction, while if $K > bT$, i.e., $\left(\frac{dE}{dl}\right)_T > 0$, E decreases during such contraction.

IV. THE MOLECULAR SIGNIFICANCE OF $\left(\frac{dE}{dl}\right)_T$ FOR ELASTIC BODIES

From the standpoint of the mechanical theory of heat, $\left(\frac{\partial E}{\partial l}\right)_T$ denotes the change in the internal potential energy between molecules or parts of molecules during isothermal change of length. If $\left(\frac{\partial E}{\partial l}\right)_T$ is positive, then during contraction forces of attraction are satisfied, either by condensation, crystallization, or formation of exothermic linkages, etc. In the special case of the contraction of an elastically deformed body this can mean that atoms that had been pulled out of the position of least potential energy ("potential trough") by the external force, fall back into this position. The atoms may in such a case have been pulled out of their "potential trough" only by the deformation of the valency angle.

If $\left(\frac{dE}{dl}\right)_T$ equals zero, this means that the work during contraction is to be attributed to the rearrangement of the atoms; it may be said that the thermal motion alone causes contraction.

If $\left(\frac{dE}{dl}\right)_T$ is negative (and therefore $\frac{dE}{-dl}$, i.e., in contraction positive), this means that the tendency towards rearrangement into a less ordered state is so great that, during isothermal contraction, there is actually more heat absorbed than work given out. The latent heat absorbed is closely akin to heat of fusion: structures in which the atoms are in orderly arrangement become amorphous.

This view is well founded in the case of rubber. The "fusion" can be detected not only thermodynamically but also roentgenographically.

V. THE MOLECULAR SIGNIFICANCE OF $\left(\frac{dS}{dl}\right)_T$ FOR ELASTIC BODIES

As is well known, the entropy is related to the thermodynamic probability, p, which is a measure of the possibilities of rearrangement and states of motion of the molecules, by the equation

$$S = R \cdot \log_e p$$

If, therefore, S increases during stretching and decreases during contraction, this means that during stretching there is a transition from a more ordered to a less ordered state; the range of movements of the atoms becomes greater.

If, on the other hand, S decreases during stretching and increases during contraction, as is the case with rubber at moderate elongations, then during stretching the possibilities of rearrangement and motion of the whole system become more limited; the system becomes more ordered. This process may consist purely in a rearrangement, without change of energy, but may also involve a decrease in internal energy, if crystalline structures are formed with evolution of heat of crystallization.

In figures 1, 2, and 3 the stress–temperature curves for phosphonitrilic chloride (20), vulcanized rubber (16), and an elastic band (17) (*Ligamentum nuchae* of the ox) are shown. It will be seen that, at moderate degrees of extension and at temperatures above 315° Absolute, the stress–temperature curves determined with falling temperatures (upper curves) pass through the origin (i.e., the stress increases in proportion to T). Hence it follows, from what has been said above, that during a change in length no change in energy occurs.

The retractive stress is thus of a fundamentally different kind from the elastic stress in a strained crystal or in strained glass, the atoms of which are pulled, by stretching, out of their "potential trough" into positions of higher energy. *In the rubber-like state, during elastic deformation within large ranges of temperature and elongation, only the molecular arrangement changes, becoming, as a result of stretching, more regular through orientation and therefore thermodynamically less probable. The thermal motion then again restores the unordered state of greatest probability as soon as the external force which produces the deformation allows this.*

This nature of the retractive force, which distinguishes rubber-like bodies from other bodies, we consider to be the best characteristic of the rubber-like state of aggregation.

We see, moreover, that in the case of moderately vulcanized rubber the curves obtained with rising and with falling temperatures coincide, whereas with other types of rubber and with phosphonitrilic chloride the rising-temperature curve lies below the falling-temperature one. This arises, as can also be shown by x-ray analysis, from the fact that at high temperatures no crystalline phase is present. As the velocity of crystallization of these substances is very low, if the material is rapidly cooled, then the proportionality between stress and absolute temperature characteristic of an amorphous body is obtained. If, now, at constant temperature and

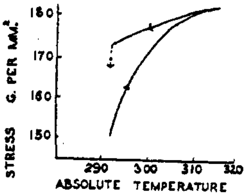


FIG. 1. Stress-temperature curve for polyphosphonitrilic chloride

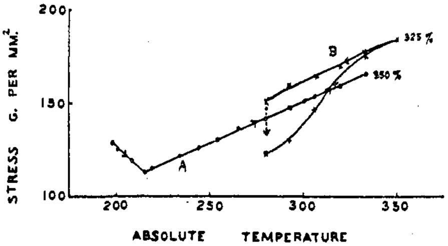


FIG. 2. Stress-temperature curves. A, rubber vulcanized with 8 per cent sulfur; no crystallization. B, lightly vulcanized rubber; gives crystal interferences on stretching.

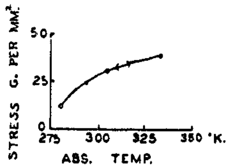


FIG. 3. Retractive stress in an elastic band at 10 per cent elongation in relation to temperature

deformation slow crystallization occurs, K decreases; if the material is again heated, heat of fusion is absorbed. Thermodynamically it follows that such a partially crystalline body takes up energy of fusion during isothermal contraction also.

VI. THE STATE OF AGGREGATION OF RUBBER-LIKE BODIES (24)

According to the above, contraction arises from the tendency of the "ordered" system to change into a less "ordered" one. The disorientation is not possible without macroscopic contraction; this forces us to the assumption that atomic groups in the oriented state cannot disorient themselves as do dipoles of a liquid, oriented by an electric field, upon the disappearance of the field. They must consequently be linked together by strong bonds in the direction of stretching. From this it follows that the rubber-like body is built up of "chain molecules." The process of orderly arrangement consists in the stretching out and parallel orientation of these chains.

Thus, even without knowing the chemical constitution, it is possible from the thermoelastic behavior of a rubber-like body to draw conclusions regarding the type of molecule known as "chain molecule."

The stretching out of the chains during elongation, moreover, compels us to assume that in the rubber-like state the atoms or atom-groups in adjacent chains can slip past each other, like the molecules in a viscous liquid. In the other direction they are firmly attached to two adjacent atoms or atom-groups. One may therefore characterize the rubber-like state thus: *that an atom or atom-group is "fixed" in bonds like those that occur in solid bodies and are responsible for their high internal friction* ($\eta > 10^{11}$ C.G.S. units) *and in the other two dimensions is "fluid," i.e., linked with the remaining neighbors by bonds like those that occur in liquids and are responsible for their viscous properties* ($\eta < 10^{8}$ C.G.S. units).

In this way the position of the rubber-like state between the liquid and solid states is made clear. We consider it incorrect to speak of two phases, because the conception of a phase requires that a great number of molecules go to make up one liquid or one solid phase. A solid phase may appear alongside the rubber phase only when rubber-like bodies of class A are stretched, but, as already pointed out, it has nothing to do with the rubber-like state. Moreover, there is no ground for the assumption that in purely rubber-like bodies groups of chains, or parts of chains, are bound together into distinct aggregates, termed micelles. Neither can one speak of intermicellar fluid. It would appear incorrect, moreover, to describe rubber-like bodies as anisotropic solids, because the anisotropy is exhibited only in molecular dimensions; macroscopic anisotropy appears only when the body is deformed.

VII. THE INTERNAL FRICTION OF RUBBER-LIKE BODIES. VULCANIZATION

The internal friction during small deformations of small speed has recently been determined by van der Wyk (31) from the damping of torsional oscillations of slightly stretched rubber threads. At the same temperature masticated and vulcanized rubbers show no appreciable difference. Both have a viscosity of the order of magnitude of 10^6 C.G.S. units, so that here the internal processes in the materials cannot be very different; the chain elements slip past one another.

Stretched specimens show a strong anisotropy; perpendicular to the direction of stretching the material is plastically deformable, e.g., a stretched round rubber thread can easily be pressed flat (13), whereas plastic deformation in the direction of stretch, e.g., flowing beyond a certain degree of deformation, encounters a very great frictional resistance, many powers of 10 greater than the former one. Now this second type of friction is very different in the two kinds of material: while masticated rubber continues to flow when subjected to considerable deformations, in the case of vulcanized rubber the frictional resistance is so great that no such plasticity can be observed.

These phenomena can be explained as follows: Whereas in lateral deformation only chain elements slip past one another, in a longitudinal displacement the whole stretched-out chain, i.e., *all* the elements in the chain, must be displaced relative to the adjacent chains. Here, therefore, the frictional resistance is a direct function of the length of the whole chain, which in masticated rubber has a finite value, whereas vulcanized rubber consists of a network of "infinitely long" chains chemically bound together. The bonds are formed by sulfur bridges (21), the nature of which has recently been established as C—S—C linkages (19).

The shorter the chain length, the less is the friction in the direction of stretching and the more quickly does the stretched rubber-like body "relax." In the case of substances with relatively short chains, therefore, the elastic properties can only be observed in deformations of short duration and small magnitude. Substances with still shorter chains form fluids.

On cooling below a temperature that depends on the material, most rubber-like materials change slowly into the amorphous solid state, and some (guttapercha) into the crystalline solid state.

The change from rubber-like state to solid amorphous state does not take place suddenly on cooling, as at a transition point. The rubber-like body at first becomes more viscous, and contraction becomes slower or even practically ceases. The friction between the chain elements, as measured by the damping of oscillations, increases considerably. Below a certain temperature the body breaks when subjected to considerable mechanical deformation.

The frozen pieces can still be stretched a little, but the atomic or molecular process that takes place during this stretching is now essentially different in nature from that occurring during stretching in the rubber-like state; during stretching in the frozen state the internal energy is increased, the atoms being pulled out of their "potential troughs."

VIII. THE NATURE OF CRYSTALLIZATION BY STRETCHING

As has been pointed out above, during the stretching of substances in class A and of certain substances in class B there are produced structures with lattice-like arrangement, the formation of which can be recognized roentgenographically and thermodynamically. Now many substances consist of a loose network of chains chemically bound together; to this class belongs, for instance, vulcanized rubber, the chains of which are bound into a network by sulfur bridges, so that individual unattached chains ("chemical molecules") practically do not exist, and the whole rubber mass can be considered as one gigantic molecule. In these cases the zones of lattice-like arrangement are smaller in the direction of stretching than corresponds to this chemical "giant molecule"; only parts of the latter are crystallized, other parts being still amorphous. We consider that also in rubber-like bodies containing molecules of finite size, crystallization, at least initially, affects only parts of the chains.

When crystallites appear, it is justifiable to speak of two "phases." The equilibrium between the crystalline and rubber-like phases depends on the temperature and the degree of strain; the greater the strain, the higher is the temperature at which the crystalline phase disappears. This is easily explained by the fact that the strain itself leads to a particular arrangement, different from random orientation, so that the entropy difference, ΔS, between crystalline and non-crystalline phases decreases. If the heat of fusion for rubber is not greatly dependent on temperature, then, according to the equation

$$\Delta E = T\Delta S$$

(where ΔE = heat of fusion and ΔS = change in entropy by fusion) T, the fusion temperature, must rise when ΔS is reduced.

It must further be assumed that with chemically pure substances, i.e., substances constituted by molecules of identical length, provided all chains undergo equal strain there is, corresponding to any given strain, a fusion point. Only at this fusion point do the rubber-like phase and crystal phase coexist. Observations on this point are lacking, and, moreover, would be difficult on account of the slowness of crystal formation, as has recently been pointed out by Thiessen (29). With impure rubber-like bodies such as vulcanized rubber, on the other hand, a fusion range is to be expected.

A process analogous to the "fusion" of stretched and crystallized rubber, fibrous sulfur, etc. (14) is the contraction of tendinous fibers and elastoidin fibers on heating, whereby they change over to the rubber-like state (Rollet's phenomenon). Here also the fusion point is raised by strain, an effect which has been exhaustively studied by Wöhlisch (32) and recently by Fauré-Fremiet (2).

IX. THE LINKAGE POINTS

In the crystalline structures formed by stretching, the chain elements are held or linked together by the lattice forces, so that slippage no longer occurs. At these points of linkage the chains will therefore behave as though they were firmly joined or "knitted" together. As a result the plasticity of the rubber-like body will be reduced. If these linkages are destroyed, a change which may be brought about by raising the temperature, the retractive force in the oriented chains suffices to overcome the friction of the whole chain; the rubber relaxes and the elastic deformation changes to a permanent plastic deformation. As is well known, this is made use of in the rubber industry when crude rubber is milled above its highest fusion temperature and pressed in molds. By adding solvents, also, the fusion point can be lowered and hence the plasticity increased. Conversely, at low temperatures there occurs a phenomenon that recalls vulcanization, and may be described as vulcanization by cold; the crystalline linkage points are increased in number by the cooling.

As already stated above, there are present in vulcanized rubber sulfur bridges which bind the chains together. These permanent chemical bonds are not sensitive to temperature and also cannot be broken by solvents; they prevent, as is readily understandable, plastic deformation even at elevated temperatures. Precisely analogous phenomena are shown by other polymers when their chains are bound together into a network, as, for instance, in the case of collagen fibers by formaldehyde (16).

Now when rubber is vulcanized with a small amount of sulfur, this does not suffice to bind all the chains into a network. Instead, there is produced a rubber-like body in which a number of unattached chains are embedded in a network of chains chemically bound together. An "unvulcanized" system and a "vulcanized" system are thus intermingled. Such mixed systems have been studied, with reference to their elastic and viscous properties, by Ferri (17). On stretching, both systems are at first subjected to stress; the unvulcanized chains, however, are then able to slip past each other, disorient themselves, and relax, while the net-like system remains in the stressed condition. If the rubber is stretched further, these phenomena reappear; the stress increases and then falls off again owing to relaxation. On removing the external tensile force the vulcanized system contracts and thereby compresses the relaxed unvulcanized system, so that an equilibrium is set up between the contracting network and the compressed free chains. These free chains can relieve themselves of the compression by gradual relaxation, so that the body continues to contract very slowly, or "creep back," until the original state is regained.

If such a rubber is allowed to remain under the influence of a constant stress, e.g., a weight, its length continues to increase for a considerable time, that is, it "flows." Finally, however, when its net system is fully extended, the increase in length ceases, whereas an unvulcanized amorphous rubber would continue to flow or else would break.

Mixed systems of interlinked chains (networks) and free chains appear to us interesting, because during passive extension they show the same behavior as smooth muscles of the lower animals. The plastic and elastic properties of these have recently been fully described by Jordan (7). After what has been said above it is not necessary to point out that we do not share Jordan's views regarding the process of relaxation, in which he considers that an intermicellar liquid and micelles play a part. We believe rather that muscles are to be regarded as a system of interlinked and free protein chains.

X. SWELLING AGENTS

If a rubber-like body is subjected to the action of liquid substances which exert on the atoms of the chain elements a force of attraction equal to or greater than that between the atoms themselves, the molecules of the liquid penetrate between the chains; the volume of the rubber-like body increases, that is, it "swells." If the chains have a finite length, they gradually become entirely surrounded by the solvent, and the swollen mass is transformed into a solution. If they are joined together by bridge-like bonds the swelling is limited; penetration of the liquid is possible only up to a certain volume increase, that is, up to the point where the network is fully extended.

Swelling agents lower the fusion point of crystalline chain polymers and the softening point of amorphous ones. By means of suitable swelling agents it is possible almost as a general rule to convert solid substances consisting of chain polymers into the rubber-like state. As examples we may quote the action of glycerol on dry gelatin, by which the elastic hectograph compositions are produced, the action of formic acid on silk (22), and of formamide on tendinous fibers. In the elastic fibrils of living organisms a certain water content is necessary to produce the rubber-like properties.

XI. CONSIDERATION OF THE FORM AND MOVEMENTS OF THE CHAINS IN THE RUBBER-LIKE STATE

As has been stated above, it follows from the elastic properties that the chains are flexible and can assume various forms. In spite of the bonds in the chain the chain elements are movable relative to one another. This conclusion is supported by the following fact: Both polyphosphonitrilic chloride and polymeric sulfur are formed, with absorption of heat, from the lower-molecular ring compounds $(PNCl_2)_3$ and S_8. The entropy content of the polymerized substances is therefore greater than of the rings. From this it follows that atoms or atom groups have more possibilities of rearrangement than in the rings; the chain elements are more mobile than in the rings (15).

Estimations of the form of the whole chain in the isotropic rubber-like state have been undertaken by Guth and Mark (4) and by Kuhn (11). The latter considers that the most probable form is a very loose ellipsoidal skein, which is, so to speak, "dissolved" within a mass formed by the neighboring chains. "The chains thus interpenetrate one another in a complicated manner."

The statistical calculations undertaken by Guth and Mark and by Kuhn showed that in the unoriented state the distance between the two ends of a chain consisting of n members each of length z lies between $z \cdot n^{\frac{1}{2}}$ and $z \cdot n^{\frac{1}{3}}$, whereas the chain when stretched out has a length of $z \cdot n$.

XII. CONCLUSION

A theoretical inquiry into the state of aggregation of rubber-like bodies seems to us to be of interest, not only in relation to the technical importance of rubber, but even more because of its close relation to biological questions. Properties characteristic of the rubber-like body are found in many animal tissues; reference may be made, for instance, to the elastic fibers, to the astonishingly high elastic extensibility of red blood corpuscles, which according to Seifriz (26) can be reversibly extended to many times their original size by means of the micromanipulator, and to the extensibility of the protoplasm of amoebae, observed by Seifriz. These systems, like all living systems, are subject to the same physical and chemical laws as non-living substances. In general it is easier to study the laws governing the non-living, more amenable materials. There is therefore ample justification for the task of first studying the laws governing chemically defined rubber-like bodies, in order subsequently to be able to apply these laws to biological problems.

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