

CROSS-LINKING IN POLYMERIC SYSTEMS

By DR. G. F. BLOOMFIELD

THE mechanical properties of a natural or synthetic polymer are profoundly affected when the van der Waals' intermolecular forces are supplemented by stable chemical linkages (cross-linkages) between the polymer molecules. In synthetic polymers, cross-linking may generally be brought about either as an essential part of the polymerization reaction, or by chemical modification of the polymer subsequent to polymerization; but cross-linking in natural rubber can only be accomplished by the latter method. Although cross-linkages in synthetic rubbers could be introduced during polymerization if desired, they are, in fact, excluded so far as possible; hence, as with natural rubber, it is necessary to carry out the cross-linking reactions on the polymer itself. In a recent series of lectures at the Royal Institution, London, various types of cross-linking mechanisms and their effect on the properties of polymers were discussed. Dr. H. P. Staudinger dealt with the cross-linking of vinyl polymers, the present writer discussed the structural modification of high polymers by vulcanization, with particular reference to rubber, and Dr. L. R. G. Treloar described the relation of mechanical properties to the degree of cross-linking in rubbers. Phenol-formaldehyde resins, in which the role of cross-linking reactions is rather less clear, were surveyed by Mr. E. G. K. Pritchett. My thanks are due to the board of the British Rubber Producers' Research Association for permission to contribute to this series of lectures and to prepare the following summary of them.

Permanent cross-linkages prevent irreversible flow and so contribute essentially to the reversible character of a deformation. Resistance to plastic flow, to thermal deformation and to solvents is thereby increased. A low degree of cross-linking, that is, less than one cross-linkage per polymer molecule, is insufficient to impart any real resistance to deformation, since the interlinked molecules still behave essentially as a linear, although highly branched, molecule; but as soon as two or more cross-links per molecule are introduced, there results a network in which flow is impeded. A high degree of cross-linking, on the other hand, leads to a highly rigid structure.

In order that rubber-like elasticity may be realized, some compromise is necessary between flow and rigidity, excessive cross-linking leading to a complete loss of rubbery characteristics.

Vinyl polymerization provides a useful means of studying the effect of cross-linking on the physical properties of polymers, particularly the flow properties, if the second-order transition temperature, T_m , can be taken to indicate the onset of viscous flow. A close relation between T_m and the average number of vinyl monomer molecules between cross-link junctions can be established. Cross-linking may be accomplished either by co-polymerizing bi- and tetra-functional monomers (for example, styrene with divinyl benzene, methyl methacrylate with allyl methacrylate), or by chemical reaction of a linear polymer containing reactive substituent groups with a substance of low molecular weight (for example, a copolymer of methyl acrylate and maleic anhydride is treated with ethylene glycol). In the first category the properties of the product may range from solu-

bility and fusibility to complete insolubility and infusibility, depending on the relative amount and on the nature of the cross-linking agent in the copolymer. Although in its initial stages the process of cross-linking with tetra-functional monomers can be interpreted by the kinetics of co-polymerization as applied to bifunctional monomers, where the relative amounts of the monomers and the relative reactivity of their double bonds are the determining factors, a full kinetic interpretation becomes extremely difficult, once inter- and intra-molecular reactions between polymer chains occur as part of the growth process in addition to the four growth reactions which are possible between polymer radicals and monomers. Fundamental differences in the polymerization mechanism arise when the degree of cross-linking is sufficient to give a gel due to a three-dimensionally interlinked network structure, for although the polymerization-rates are not significantly changed when the concentration of the cross-linking reagent is low, there is a marked increase in rate, coinciding with the appearance of the gel, when more of the cross-linking component is used.

Considering that termination is a bi-molecular reaction with respect to polymer radicals, the high viscosity of the medium—which is infinite once gel formation has occurred—will restrict diffusion of, and reduce collision between, polymer radicals, thus reducing the termination-rate; while propagation, involving diffusion of, and collision with, monomer, is little affected.

In order to exercise some measure of control over cross-linking by copolymerization, it is desirable to select types of double bond of widely different reactivities within the cross-linking molecule, the ideal being to produce a linear molecule by polymerizing the vinyl bonds, and then to promote a cross-linking reaction involving the less reactive bonds by a rather more drastic treatment. In practice, polymerization is first conducted to a point short of gelation, and the resulting syrup is used for casting or impregnation. An outstanding advantage of the new technique is that it requires no high-pressure equipment, and is accordingly very suitable for the fabrication of structures of considerable size.

A particularly undesirable form of cross-linking in vinyl polymerization is that responsible for 'popcorn' formation, in which small particles resembling popcorn grow rapidly with considerable volume expansion. 'Popcorn' formation is determined mainly by temperature and the proportion of cross-linking agent, consequently control involves both of these two factors. 'Popcorn' can itself initiate fresh 'popcorn' growth in virtue of its hydroperoxide content, or as a result of electronically stabilized radicals becoming reactive.

In cross-linking by chemical modification subsequent to polymerization, it is necessary that the polymer should contain functional groups (for example, ethylenic linkages) or reactive substituents (for example, halogen, hydroxyl, carboxyl).

An important aspect of cross-linking by chemical reaction is that comprising the whole field of rubber vulcanization; in fact, any reagent which is capable of providing intermolecular linkages between two or more polymer molecules is capable of vulcanizing rubber. The properties of the resulting vulcanizate, however, depend not only on the nature and number of the cross-linkages, but also on the possibility of side reactions and on the treatment necessary to promote reaction, and consequently they vary widely.

Rubber vulcanizing agents fall into two classes: those giving rise to radical reactions leading to carbon-carbon cross-linkages, and those which affect bridging through the agency of a bifunctional atom or molecule which itself forms the cross-linkage. The simplest example of carbon-carbon linking is provided by photogelling; cross-linking reactions of benzoyl peroxide, diazoaminobenzene and other reagents which decompose thermally to give free radicals are believed to follow a similar course. Bifunctional reagents include dinitroso compounds, azodicarboxylates, hydrogen sulphide, dithiols, sulphur chloride, and, most important in technical rubber practice, sulphur. The essential cross-linking reaction of sulphur consists in the establishment of a polysulphide bridge between two of the originally unsaturated molecules, with loss of one of the original double bonds and a displacement of the other. A necessary prerequisite of a cross-linking agent is that it shall react intermolecularly. The 1:5 diene system in rubber is, however, particularly prone to form intramolecular cyclic linkages when the reagent contains only one or two atoms between its reactive ends, and sulphur is no exception. The formation of tetrahydrothiopyrans has been demonstrated in the reaction of sulphur with small polyisoprenic molecules, and the low efficiency of sulphur as a cross-linking agent for rubber is undoubtedly to be attributed, at least in part, to its participation in cyclic linkages of the tetrahydrothiopyran type. A contributory cause of the low efficiency of sulphur is its participation in polysulphide rather than monosulphide cross-linkages. Rubber vulcanization is consequently very susceptible to small amounts of auxiliary substances capable of promoting intermolecular rather than intramolecular linkage, or capable of promoting monosulphide rather than polysulphide cross-linkages. Certain accelerated vulcanizates accordingly exhibit a much higher efficiency of cross-linking, although they still fall short of the theoretical maximum of one cross-linkage for each sulphur atom incorporated.

From the theoretical point of view, a vulcanized rubber is visualized as a three-dimensional network of molecules, the mechanical properties of which may be calculated by the methods of statistical thermodynamics. The physical basis of this approach is the assumption that the individual chains (or portions of molecules between successive junction points) are in a state of random thermal fluctuation of form, by virtue of the relative freedom of rotation about single bonds in the chain. This kinetic basis provides a reasonably satisfactory quantitative background for such physical properties as the form of the stress-strain relations in any type of strain, the effect of progressive vulcanization on tensile strength, the optical double refraction due to strain, and the principal phenomena of swelling in diverse liquids. By the use of certain simplifying assumptions it is possible to derive the following force-extension curve for a vulcanized rubber:

$$F = (\rho RT/M_c) (\alpha - 1/\alpha^2), \quad (1)$$

where F is the tensile force, referred to the original cross-section, α is the ratio of the stretched to the unstretched length, ρ the density and M_c the 'molecular weight' of the chains between successive points of cross-linkage. Two interesting features of this equation are worth noting: first, the form of the stress-strain curve is determined by $(\alpha - 1/\alpha^2)$, and should therefore be the same for all rubbers, whatever their chemical constitution; and secondly, the

modulus ($\rho RT/M_c$) should be inversely proportional to M_c , the chain-weight between points of vulcanization, or alternatively, directly proportional to the number of cross-links.

Generally speaking, these theoretical predictions have been borne out experimentally. For a series of rubber-sulphur vulcanizates Gee observed a direct proportionality between modulus and percentage of combined sulphur, while Flory, in a comprehensive investigation of a range of butyl rubbers, obtained close agreement with the slightly modified formula

$$F = \rho \frac{RT}{M_c} \left(1 - \frac{2M_c}{M}\right) (\alpha - 1/\alpha^2) \quad (2)$$

(M is molecular weight before vulcanization, M_c is molecular weight between junction points), in which the effect of terminal chains connected to the network at one point only is allowed for.

The swelling of rubbers by liquids is a phenomenon closely related to the mixing of two liquids. For a good swelling agent it is found experimentally that the absorption of the solvent is accompanied by very little change of energy. It is, however, accompanied by a very large change of entropy. Equilibrium swelling is achieved when the entropy increase due to the absorption of an additional small quantity of liquid is balanced by the entropy decrease due to the expansion of the elastic molecular network. Both the entropy of mixing and the network entropy can be calculated, and in this way it is possible to predict quite accurately how the maximum swelling will depend on the degree of cross-linking. Since the modulus also is determined by the degree of cross-linking, it follows that there should be a close relation between the modulus and the maximum swelling for a series of rubbers of different degrees of cross-linking. The quantitative relation worked out by Flory indicates that the modulus should vary inversely as the five-thirds power of the maximum swelling ratio—a relation which was found to be very closely borne out by Flory's data for butyl rubbers.

A phenomenon which is at first sight rather surprising, and for which, until recently, no explanation had been given, is the rapid fall in the breaking strength of natural rubber vulcanizates which occurs when the degree of cross-linking is increased beyond the optimum value. In a recent publication by Gee, evidence is brought forward which indicates that the effect may be explained in the following way. With increasing cross-linking the modulus continuously increases, and at the same time the elongation at break tends to fall progressively. But with reduced extensibility there is reduced molecular orientation and therefore very probably a reduction in the degree of crystallization. It is this reduced crystallization which gives rise to the reduction in tensile strength, since the crystallites have the effect of introducing strong binding forces between the molecular chains.

In the field of thermosetting resins, the role of cross-linking reactions is by no means so well established as in vinyl polymers and in rubber. Although the conception of cross-linking by methylene groups at the p -positions of the benzene rings is widely accepted, there are difficulties in the general application of this principle, since it is not at all certain that hydroxyl groups may not also be involved in the thermosetting reaction; and it is noteworthy in this respect that p -cresol resins show some thermosetting properties. Models indicate that methylene-linked structures are extremely rigid, since rotation of the

benzene rings is very restricted sterically; thermo-setting linkages may possibly involve only a few of the benzene rings, so giving a plausible explanation of the low tensile strength of phenolic resins. An entirely new conception proposed by E. G. K. Pritchett envisages a mechanically interlinked rather than a chemically cross-linked structure, the extreme rigidity rendering the substance insoluble and infusible.

SALMON AND ANIMAL MIGRATION

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MORE than two thousand years ago, Aristotle wrote that all the actions of animals are for breeding, for feeding and to avoid extremes¹. Clearly such motivations of migration satisfy those who ask why animals migrate; but have they been verified and are they verifiable? Are they still accepted as explanations of migration, the only problem being to discover how the animal can accomplish wonderful feats? Has such an attitude been successful in elucidating migration? The statements that for birds "this question has been extolled as a mystery of mysteries"² and that for the salmon migration is accomplished by "an instinct which man cannot comprehend"³ are not reassuring.

If the matter is not yet clear, it may be because the proper approach has not been used. Perhaps migration should be considered merely as wandering, as was the original meaning. Facts against the prevalent ideas have long been known⁴; but no attempt seems to have been made to develop theories to include them, except as divorced from 'true migration', which has the idea of purpose either of the animal or of 'Nature'. It is not clear how we can verify the animal's purpose, and, as to Nature's purpose, it may be a mistake to assume that the animal's behaviour should be useful for survival, rather than merely not incompatible with survival of some of the race somewhere. If migration is merely wandering, that is, changing the place of abode, the problem is when and whither will an animal wander in view of its nature and of the conditions to which it is exposed. There has been a growing tendency to treat the matter thus objectively, which may permit accurate prediction.

For more than a decade, the Fisheries Research Board of Canada has been intensively studying the salmon (*Salmo salar*) as a somewhat representative fish. This study has provided the main facts with which we are attempting to develop a true science of fish migration.

No simple method of salmon behaviour will permit accurate prediction, since they behave most variously, as the following examples show. They may or may not spawn as parr before moving from the locality where they were spawned. On metamorphosing into smolts in the spring, they fail to spawn in that year and may or may not spawn in subsequent years up to the fifth. Usually, parr remain in streams, smolts and kelts (adults after spawning) descend, and near-spawning adults ascend; but salmon may or may not descend to or ascend from the sea as parr⁵, as smolts, as near-spawning adults and as kelts⁶. Clearly, the idea that their migrations are between breeding

grounds in rivers and feeding grounds in the sea is inadequate. Some differences in behaviour have been ascribed to differences in original nature (sub-species or races); but for none of these has the original nature of the individuals been shown to be different, while correlations with environmental differences are evident and experiments fail to show that offspring of those behaving differently will behave differently under the same conditions, for example, for descent to the sea, that is, "migratory and non-migratory races"⁷ or for time of return to streams, that is, "early and late running races"⁸.

One theory that fits the facts, but that can be only part of the complex whole, is quite simple. It is that in the rapid water of a stream the fish is carried down (as it must be more or less) in its descending, and swims actively up (as it must) in its ascending migration, these being the only directions in which stream fishes can migrate. The well-known upstream orientation of fishes, or rheotaxis, which may or may not be elicited by the flowing water, depending upon the conditions, and the more or less active swimming of the fish are all that the theory requires. Underyearling salmon have been found to vary sufficiently to separate into two groups when placed in a rather strong shallow current—those that ascend and those that descend—but they all head upstream. Similarly, when with a strong freshet in the rivers the salmon in the sea left the east coast of Sutherland near Brora for the rivers, 'droppers', that is, salmon that had ascended the rivers and remained there for some time, but had dropped down again, appeared in coastal nets⁹.

When entering the smolt stage for which descent is typical, salmon behave most variously. With higher, that is, swifter water, more descend^{10,8}. Some descend quickly, some very slowly, and some fail to descend; yet they would all leave the stream in a few hours if they merely kept up from the bottom and headed downstream. Smolts marked as they left Forest Glen Brook for the large North-East Margaree River, Nova Scotia, in the spring of 1938, arrived at a trap fifteen miles down that river in from 1 to 28 days or more. It is judged that they all could, if headed right, have descended in 12 hours. In swift water they descend tail first swimming vigorously upstream, and they sometimes ascend rapids, as may be seen when they near a trap placed in swift water. That in slow water descending fish all head downstream into a trap may mean nothing more than that all the others, if swimming faster than the water flows, are certain to be moving upstream, since the narrowness of the stream prevents movement any distance in directions other than up and down. In a lake, roaming near the surface would be apt to take them near enough to the outlet for the current to act.

In September and October of 1945, smolts were still to be found above beaver dams in Holmes Brook near Moncton, New Brunswick, in spite of freshets that were thought to have brought them down. This finds explanations in observations by Mr. C. W. Andrews in trapping smolts on the neighbouring Pollett River. With quite low water in 1944, smolts known to be in the pool above the trap failed to descend during the forty-three subsequent days of operation of the trap and no rise in water. In late evening he saw them to have descended to the brink of a shallow rapid, and they moved back up to the pool by morning. Clearly, when near the surface and down to this rapid in the