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Crosslinking of Polymers by Radiation*

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Summary

Early work showed that many polymers become crosslinked following exposure to high energy radiation—typically high energy electrons or gammas. Subsequent research has sought to answer a number of basic questions on radiation mechanisms. At the same time applications have been sought successfully in a range of specialist materials.

One of the great advantages of radiation treatment is that it enables useful chemical reactions to be initiated in the solid state. The precise mechanisms involved are still not generally agreed, but appear to depend largely on the interaction of radicals which, to promote crosslinking, must be mobile. A series of reactions occur between the initial absorption of radiation and the final chemical change, and it is possible to intervene in several of these stages to modify the final product. This type of study shows considerable relevance to the problems investigated in radiobiology. Other aspects of importance are the crosslinking of polymers in solution, the radiation treatment of single crystals of polymer, and the use of additives for reinforcement.

After an initial period, radiation processing has become an established industrial procedure, aided largely by the rapidly reducing cost of high energy radiation. Its wider use must be largely determined by the discovery of new applications in which its unique advantages can be fully utilised.

Introduction

The study of crosslinked polymers offers a series of intriguing problems in mathematics, physics and chemistry. In the last decade the use of radiation to achieve such crosslinking has advanced from a scientific discovery to a very practical industrial process, and the range of its applications is far from exhausted. At the same time it is a convenient research tool in such subjects as radia-

tion physics and chemistry; radiobiology; solid state chemistry and lastly—but far from least—in polymer science.

In the early days of radiation research it was felt that the very high energy available in each gamma photon or fast electron, greater by a factor of some 10^5 than the energy of chemical bonds, could initiate new types of reaction, though at very high cost. In fact it appears that high energy radiation, at least in the present context, can be considered as a convenient means of producing radicals, ions and free electrons throughout the body of the irradiated material, and their subsequent reactions are similar to those resulting from chemical initiation. The main advantages of radiation reside in its flexibility; in the vast range of possible dose rates and hence concentration of reactive species; the ability to initiate reactions in solid materials and over a wide range of temperature and without additives. This means that we can separate out the initiation process from subsequent reactions.

The cost of high energy radiation for industrial processing has fallen rapidly with the advent of powerful electron accelerators, and the widespread availability of radioactive isotopes. If we take a purely nominal figure of say 10 SF per Kwh for a large-scale process including running costs, interest and amortisation (the precise figure will of course depend on the installation and its utilisation) the following simple calculation can be made.

1 Kwh = $2.25 \cdot 10^{25}$ electron volts gives $2.25 \cdot 10^{23} G$ reactive chemical species, where G is the number of such species produced per 100 ev absorbed, typically 3. Thus 1 Kwh (say 10 SF) of absorbed radiation energy will give about one mole of reactant, roughly comparable

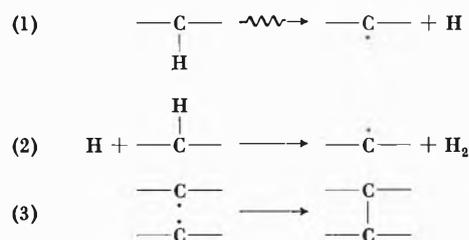
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with the cost of certain chemical initiators. For many processes this is far too high. The situation can be improved for chain reactions such as polymerisation, graft or block copolymerisation, solid state polymerisation, when the cost of initiation is a small fraction of the total, since the number of initiations required is small. Alternatively one may envisage the use of radiation for the modification of polymers, e.g. crosslinking, when a very small chemical change such as the introduction of only a few crosslinks into a high molecular weight molecule can greatly affect such properties as solubility, swelling and mechanical behaviour. These considerations are sufficient to show that choice of an industrial process suitable for radiation involves a detailed study of each individual application, with special attention being paid to the particular advantages of radiation. Several such processes have been established on a wide scale, and depend essentially on the ability of radiation to crosslink a polymer in the solid state after its shape has been determined e.g. by extrusion or moulding. Use is then made of the «memory» effect, whereby crosslinked polymer, on heating tends to return to the shape it held during radiation.

At this conference it appears appropriate to discuss several recent lines of research in which radiation has been used to crosslink polymers.

Radiation Mechanisms

The passage of high energy radiation through an organic polymer causes ionisation and excitation, and these lead to the formation of radicals and ions, as well as trapped electrons. Their presence can be revealed in various ways, for example by electron spin resonance, optical spectroscopy or thermoluminescence. Much discussion has occurred on the species responsible for crosslinking and there is evidence for both radical and ionic processes, but it is generally felt that the former reaction predominates. An important question therefore arises: are the two radicals needed to provide a crosslink formed in pairs, or are radicals initially formed scattered at random and subsequently migrate to form pairs, and if so is there any preferred pattern in this migration? It appears likely that radicals are formed initially at random (e.g. in crystalline and amorphous phases) but that the H atom liberated often abstracts a second H in the immediate vicinity—thereby providing an adjacent pair which can crosslink immediately



In other cases the H atom loses energy by collision and migrates a considerable distance before abstracting. In such cases the radicals are distributed at random and must migrate. In polyethylene it may be considered that pairs of adjacent radicals can crosslink readily in the amorphous regions due to the flexibility of the chains. Radicals in the crystalline region (which can be distinguished by e.s.r. techniques since they will be oriented in stretched material) will be largely prevented from crosslinking there by the more rigid chain structure, which prevents appropriate chain alignment. These radicals can migrate to the amorphous regions and crosslink there. If this view is correct we would expect a much higher concentration of crosslinks in certain regions of irradiated polyethylene when this is subsequently molten, but a random distribution if radiation takes place in the molten state. We have only indirect evidence of this.

Crystal Morphology

Investigations by KELLER and others on the structure of polyethylene and other polymers has shown that large well-formed single crystals (with folded macromolecules) can be formed under suitable crystallisation conditions. This runs counter to the classical micelle theory of partly crystalline polymers, and it is therefore important to discover how far the structure of bulk material (as used in industry) compares with that of these single crystals. Radiation has been used to elucidate the problem.

Experiments show that bulk polyethylene (pellets) and an agglomerate or mat of single crystals, after radiation, give essentially the same yield of radicals and of hydrogen gas. Thus the initial reactions are similar. However the density of crosslinks, as revealed by solubility measurements indicate a difference which may be as high as 10 to 1 in favour of the bulk material for the same dose. Hence most of the radicals must react in some way in single crystals without producing effective crosslinks.

If links are formed within each crystallite, between successive folds of a single molecule, then such links are ineffective as far as crosslinking is concerned. However at high doses, each molecule will no longer be linear on melting but contain a large number of loops, each comprising about 100 monomer units. These should reduce the viscosity in solution. However no such drastic decrease in viscosity is observed. We must therefore assume that most radicals formed within each crystalline region migrate to the surface, and produce a small internal link at the point of folding (loop), where conditions such as molecular mobility are more favourable. This would result in very small loops, and only a slight change in viscosity. Where two adjacent crystals have overlapping folds, a restricted amount of crosslinking is possible. Thus we may consider the true situation in

bulk material as lying intermediate between the folded crystallite and the micellar models, with some intermingling at the folds, and some degree of interpenetration of polymer chains. The degree of such interaction will depend largely on the previous thermal history of the sample.

Crosslinking in Solution

In general there are only minor differences in the efficiency of crosslinking as between polymers irradiated in the solid or in the liquid state. However considerable differences appear when polymers are irradiated in solution, either aqueous or organic. These differences are associated with the subsequent reaction of reactive species, formed by the energy absorbed in the polymer (direct effect) or in the solution (indirect effect). For example in polymers in aqueous solution, OH and e^- produced in the water may react with the polymer to give additional polymer radicals capable of crosslinking. As the polymer concentration is reduced, the number of such radicals per polymer molecule is increased for the same radiation dose. Since a gel structure begins to form at an average of one crosslinking radical per (weight average) molecule, the net effect is that the minimum dose to form such a network decreases as the concentration is lowered (i. e. as the polymer molecules are further apart).

If this process were to continue indefinitely one would expect to find gel formation at extremely low doses in very dilute polymer solutions. In fact this is not the case. Below a concentration of about 1% of polyvinyl alcohol, polyvinyl pyrrolidone or polyethylene oxide in water, the dose for gelation increases again and at about half this concentration no gel formation occurs even at very high doses. The explanation of this reversal in behaviour resides in the possibility of internal links being formed in competition with links between adjacent polymer molecules. Each internal link not only results in the loss of a potential crosslink, but in addition forces the individual polymer to take up a more contracted form, thereby further reducing its tendency to link with other molecules. Thus if C represents the average concentration of monomer units from other polymer molecules around a given unit, and C_0 the equivalent concentration of units from the same polymer molecule, then the proportion of radicals which are used in crosslinks is reduced in the ratio $C/(C + C_0)$. With internal crosslinking C_0 increases and the ratio falls. In practice some external links are formed at first, so that the irradiation of very dilute solutions results in the formation of microgel. Measurements of gelation dose as a function of polymer concentration, pH of solution, molecular weight of polymer can therefore provide considerable information on the configuration of polymer molecules in solution. Further data can be derived from the changes in viscosity, which often appear anomalous.

The research can be further elaborated by the presence in the solution of minute amounts of additives capable of acting as radical scavengers, H donors or acceptors, or electron traps. In this way the changes caused by exposure to radiation can be repaired or modified. This type of behaviour is seen in both polymeric and biological systems and constitutes an important method of investigating methods of radiation protection.

Once a crosslinked network is formed, further radiation can cause crosslinking and a contraction of the swollen gel, producing a spongy material, whose maximum degree of swelling is directly related to the radiation dose.

In organic solutions, the behaviour under radiation is somewhat different in that polymer radicals can frequently react with those produced in the solvent, giving a branched or graft polymer at the expense of crosslinks. Changes in shape of the gelation dose-concentration curve are far less sharp, and the concentration for minimum gelation dose is much greater.

A further reaction which can occur between polymer and solvent fragments may result in chain scission and a reduction in molecular weight. This aspect does not appear to have been studied in any detail.

Reinforcement

The mechanical properties of many crosslinked polymers can be enhanced by the incorporation of suitable fine particles, as for example carbon black in rubber. The mechanism of this reinforcement has been variously interpreted as due to a chemical interaction of polymer with particle giving some form of additional crosslink, or as due to a physical interference with the process of elongation under stress. This problem of outstanding importance has attracted considerable research activity without any generally accepted conclusion being reached. A major difficulty arises from the possible interference of these particles with the chemical curing process, so that series of samples with known densities of crosslinking and filler concentrations are not readily available.

When crosslinking takes place by radiation, several important simplifications can occur. The effect of crosslinking (dimerisation) occurs equally readily in low and high molecular weight compounds of similar chemical structure, so that mixtures of filler and model compounds can be irradiated to determine any interactions—which will be identical to those occurring in the high molecular weight material. Furthermore the resultant mix still remains soluble at high doses, so that the irradiated mixture can be separated by simple means for subsequent analysis. A second advantage is that whatever the chemical change, it will be proportional to dose; quantitative comparisons of physical properties then become feasible with varied and known density of crosslinking.

During the process of mastication on a mill of rubber with carbon black, a partly insolubilised mix is produced

and this formation of bound rubber is taken as evidence of a chemical surface reaction between rubber and black. It is then frequently assumed that the same reaction is continued during conventional sulphur curing to provide a more highly crosslinked network with the appropriately higher elastic modulus as deduced from the theory of rubber-like elasticity.

We may now consider a model type experiment using radiation as the curing agent. A mixture of Squalene/Phylblack E carbon is irradiated to the dose equal to that needed to produce a fully cured rubber. The radiation-induced bonding of squalene with carbon black should be comparable with that of rubber + carbon black. The degree of attachment is measured by extracting the squalene and measuring the weight increase of the carbon black due to chemically-attached squalene. The following results are obtained.

Carbon black %	Dose (megarads)	Attached squalene %	G (attachment)
10	45 in air	0.1	very small
33.3	50 in vacuum	9	1.4 to 2.1 *

* The value of 1.4 assumes that only energy absorbed in rubber is effective; 2.1 assumes that energy absorbed in carbon black also acts.

The conclusion from these measurements is that some degree of binding or linking does occur between squalene and black particles, but the *G* value (links per 100 ev) is only slightly higher than the *G* value for rubber-like links. Hence the increased modulus is not ascribable to a greatly enhanced crosslink density.

A similar conclusion is reached with dimethyl siloxane polymer, reinforced with silica powder, with various degrees of surface treatment (untreated, esterified, vinyl modified etc.). With a relatively low molecular weight silicone (50 centistokes) the adhesion resulting from high doses (46 Mrads) corresponds to *G* values of between 0.6 and 1.2. This is comparable with the efficiency in forming direct polymer crosslinks. During milling an effect similar to bound rubber is also found in high molecular weight mixes with untreated silica, but this is not increased by subsequent irradiation. The degree of reinforcement, expressed as the increase in modulus per unit dose and per unit concentration of filler has been compared for a wide range of fillers of varying size, surface and chemical nature. The major conclusion is that (with two exceptions) the reinforcement is related to particle size rather than particle nature or surface structure. For such mixes we believe that reinforcement in the sense of increased modulus is due to the presence within the network of small solid particles which prevent the molecular chains from taking up any desirable configuration, allowed in the theory of rubber-like elasticity. However it is not all certain that this interference is mainly

responsible for the enhancement of properties in rubber-carbon black mixes.

The increase in tensile strength with filler may be associated with the higher modulus in an indirect fashion. The small filler particles are available to spread the load between neighbouring chains, and since they can rotate, are able to equalise the tension. Furthermore once a tear has started to propagate, it may be diverted into a harmless direction. The improvement in tensile strength due to the presence of these fine particles in silicone polymer is quite remarkable.

Conclusion

In this review it has been impossible to give more than four instances of the manner in which radiation can be used to elucidate interesting problems involved in cross-linked materials. A number of other lines of research is being carried out which will presumably lead to equally interesting results of both theoretical and practical value to polymer scientists, students of the solid state and radiobiologists.

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