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History of the Irradiation Cross-Linking of Polyethylene

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ABSTRACT

The formation of covalent C–C bonds or cross-links between the long chains in polyethylene (PE) by means of high energy irradiation was first deduced from changes in the stress-strain curves of the PE samples after irradiations in vacuo in the heavy water pile of the Argonne National Laboratory near Chicago in the academic year 1947-48. These cross-links can be produced in the solid sample at room temperature without change of shape of the sample. Such irradiated PE samples have a "memory effect" which has led to a large-scale application of the irradiation of PE to make heat shrinkable films and tubing.

In the case of polymers such as polyethylene (PE), the formation of cross-links, that is, covalent C–C links between the long molecular chains, is of considerable theoretical and industrial importance. As shown below, the stress-strain properties and cold drawing ability are remarkably affected by the introduction of the cross-links into the material. The polyethylene becomes insoluble in hot solvents and more resistant to higher temperatures and a "memory effect" is introduced into the material. This effect, as described by Charlesby [1] in 1954 in the case of irradiated PE, means that if PE is molded into a particular shape such as film or tubing and then irradiated at room temperature with high-energy electrons or γ-rays so as to

cross-link the material, it can then be heated above the melting temperature of the crystallites in the sample, and because of the cross-links it is then in a rubbery state and while at the upper temperature can be distorted by expanding the tubing by air pressure or by stretching the film. On recooling to room temperature in its expanded state the crystallites reform and the irradiated sample is then "frozen" in its distorted or expanded state and will retain such shape until it is subsequently heated once again above the melting point, at which moment the sample spontaneously returns to its original undistorted form. It "remembers" its original shape and dimensions. This heat shrinkable propensity of the irradiated PE is similar to the heat shrinkable (but not irradiated) polyvinyl chloride previously described by Currie [2] in 1936. The great virtue of cross-linking PE by irradiation is that the links can be introduced into the material at room temperature in whatever shape the PE happens to be without significantly changing the shape or the dimensions of the sample.

My interest in studying the radiation effects in polymers arose during World War II when I was working on the Manhattan Project at the Lawrence Radiation Laboratory in Berkeley. At that time the first nuclear pile in Chicago had just gotten into operation and scientists were confronted in part with problems arising from the intense radiation emitted by the pile when operating. The stability of materials such as the insulation on electrical wiring to the radiation was an important consideration. In some of the classified reports that I had access to, I read that studies of such materials were performed by putting the materials into the pile for various periods of time and seeing what radiation damage the materials had suffered. However, no attempts at that time were being made to unravel the actual changes in the molecular structures due to the irradiation. I thought that this would be an interesting field of research.

Returning to Northwestern University in Evanston, Illinois, at the end of the war, I was fortunate to receive grants for polymer research from E. I. du Pont de Nemours and Co. (Pioneering Research Laboratory in Buffalo) and from Visking Corp. (now a part of Union Carbide) in Chicago. The Richardson Co. of Chicago also provided me with fellowship money which enabled me to take on a beginning graduate student, Donald G. Rose, who had been working at the Clinton Laboratories in Oak Ridge. We had no radiation facilities available to us at that time at Northwestern, but by making suitable application and financial arrangements we were able to get our PE samples irradiated in the heavy water pile of the Argonne National Laboratory near Chicago. The Visking Corp. provided us with 0.05 mm thick PE films which were encased in aluminum tubes with perforated holes for irradiation in air or were sealed up in quartz tubes for irradiation in vacuo. After exposure the material showed very little induced radioactivity and was safe to handle without shielding in a couple of days. The Visking Corp. also permitted us to study stress-strain properties of the irradiated PE using their Scott Inclined-Plane tensile stress machine. The latter automatically records the increase in elongation as the load increases at a constant rate.

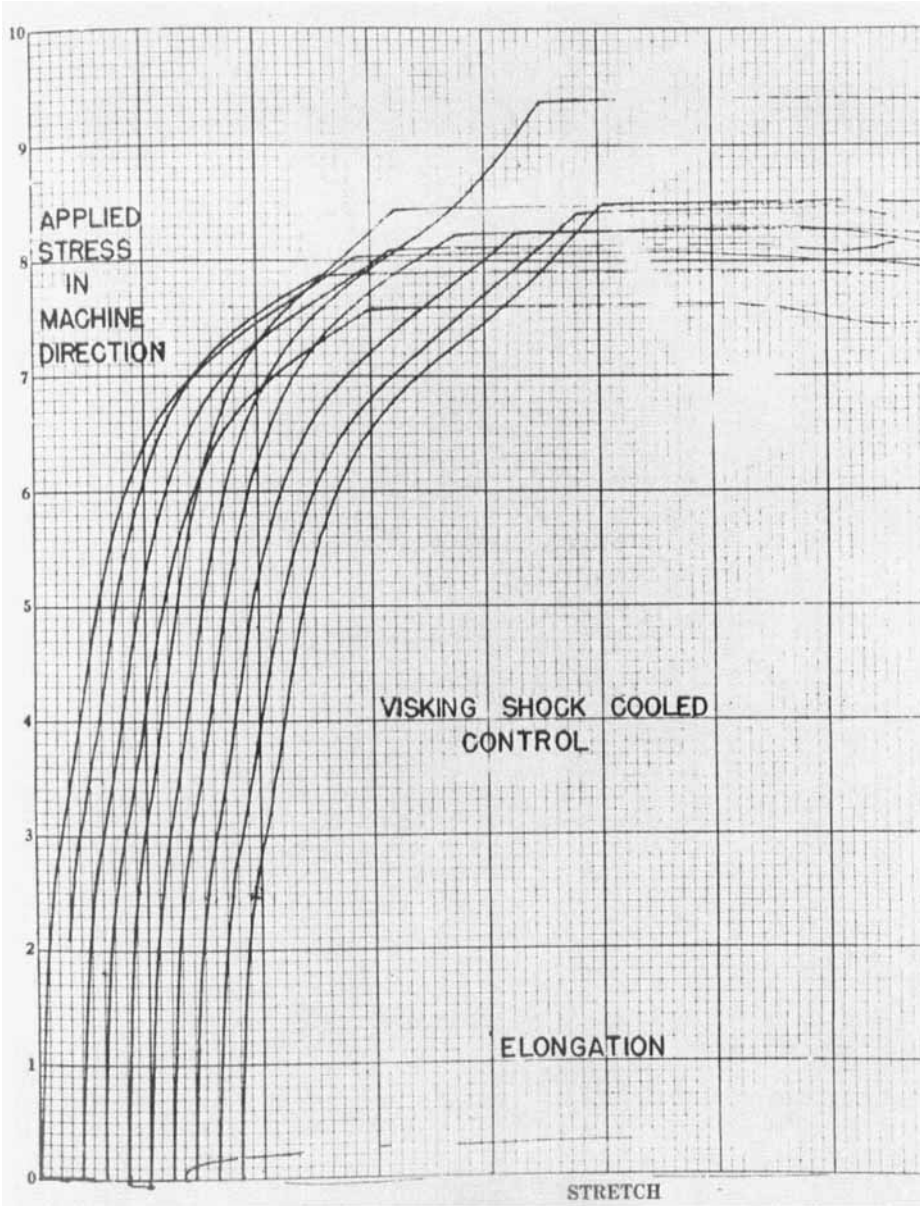

FIG. 1. Scott inclined plane tensile strength machine recordings of the stress-strain curves of polyethylene film before irradiation. Each curve represents a separate experiment.

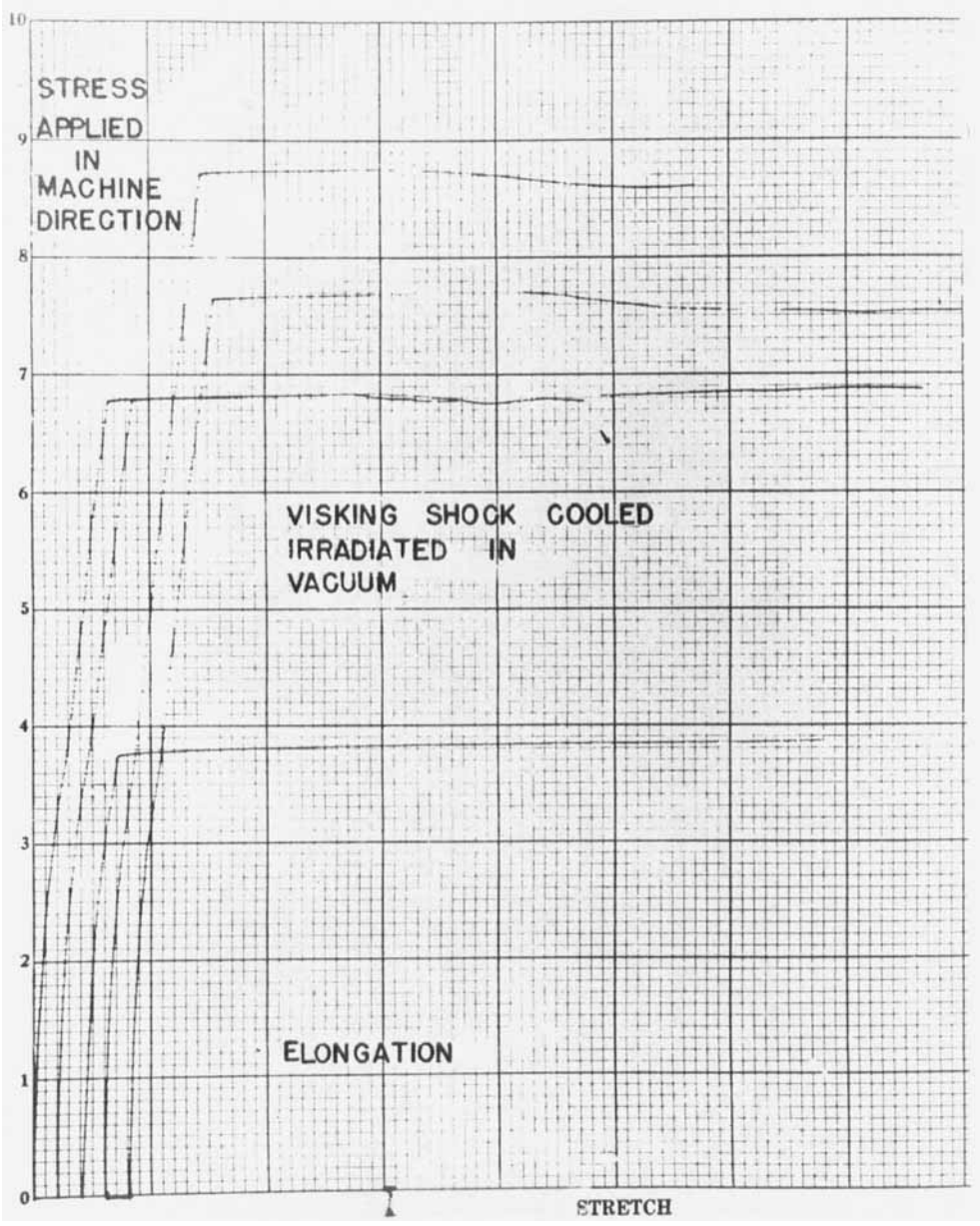

FIG. 2. Same as Fig. 1, but after an irradiation in vacuum.

Turning now to the results of the irradiation, we immediately discovered a remarkable elimination of the cold-drawing ability of the PE by the irradiation. This is shown by the curves of Figs. 1 and 2. Figure 1 illustrates the stress-strain curves of the unirradiated material. Each curve represents a separate experiment on a single strip of film which was drawn out until it broke. The breaking point is indicated by the sudden break in the curves at ordinate values of about 7.5 to 9.5. Note how much these strips of film elongated just before break. In Fig. 2 similar curves for the irradiated samples are shown. Very dramatic results can be seen in that the stress-strain curves are almost perfectly linear right up to break. In other words, the cold-drawing ability of the film was completely eliminated by the irradiation and we interpreted these results as due to the formation of interchain cross-links. Because these films were irradiated in a vacuum, oxidation did not occur and did not, therefore, affect the shape of the curves in any way. Infrared spectroscopic studies demonstrated that no oxidation had occurred for the vacuum irradiated samples.

Figure 3 illustrates the IR spectra of the irradiated and nonirradiated PE film. Note that a distinct new band of 10.4 μm wavelength (960 cm^{-1}) was produced by the irradiation. This is proof of the formation of the trans-vinylene double bond. Hence the irradiation produced internal unsaturation as well as cross-links.

These results of the first irradiation of polyethylene were presented at the September Meeting of the American Chemical Society in Portland, Oregon, 1948, Paper No. 60, Physical Chemistry Division, "The Effect of Pile Irradiation on Polythene," Malcolm Dole and Donald Rose [3]. Later a more complete presentation [4] was made at the "Symposium IV. Chemistry and Physics of Radiation Dosimetry." Technical Command, Army Chemical Center, Maryland September 1950. See also the MS thesis of Donald G. Rose, Northwestern University, June 1949.

In 1952 Charlesby [5] published the first of his important series of papers on irradiation effects in polymers, and as this paper appeared in the Proceedings of the Royal Society it received much greater recognition than the earlier work of Dole and Rose. In 1953 Lawton [6] and his group at the General Electric Research Laboratories in Schenectady irradiated PE with high-energy electrons and thus began the important work that they did there. They made use of the resonant transformer type of electron beam accelerator developed by GE which has been very important in industrial applications of irradiation to polymers. Irradiated PE was marketed by GE under the trade name Irrathene.

The most successful industrial applications of irradiation of PE have been the manufacture of heat shrinkable film by W. R. Grace and Co. (annual sales over $200,000,000 [7]) and of heat shrinkable tubing by Raychem. Corp. Irradiation is also used in the rubber industry to improve the "green strength" of automobile tire components during tire manufacture as described by Hunt and Alliger [8].

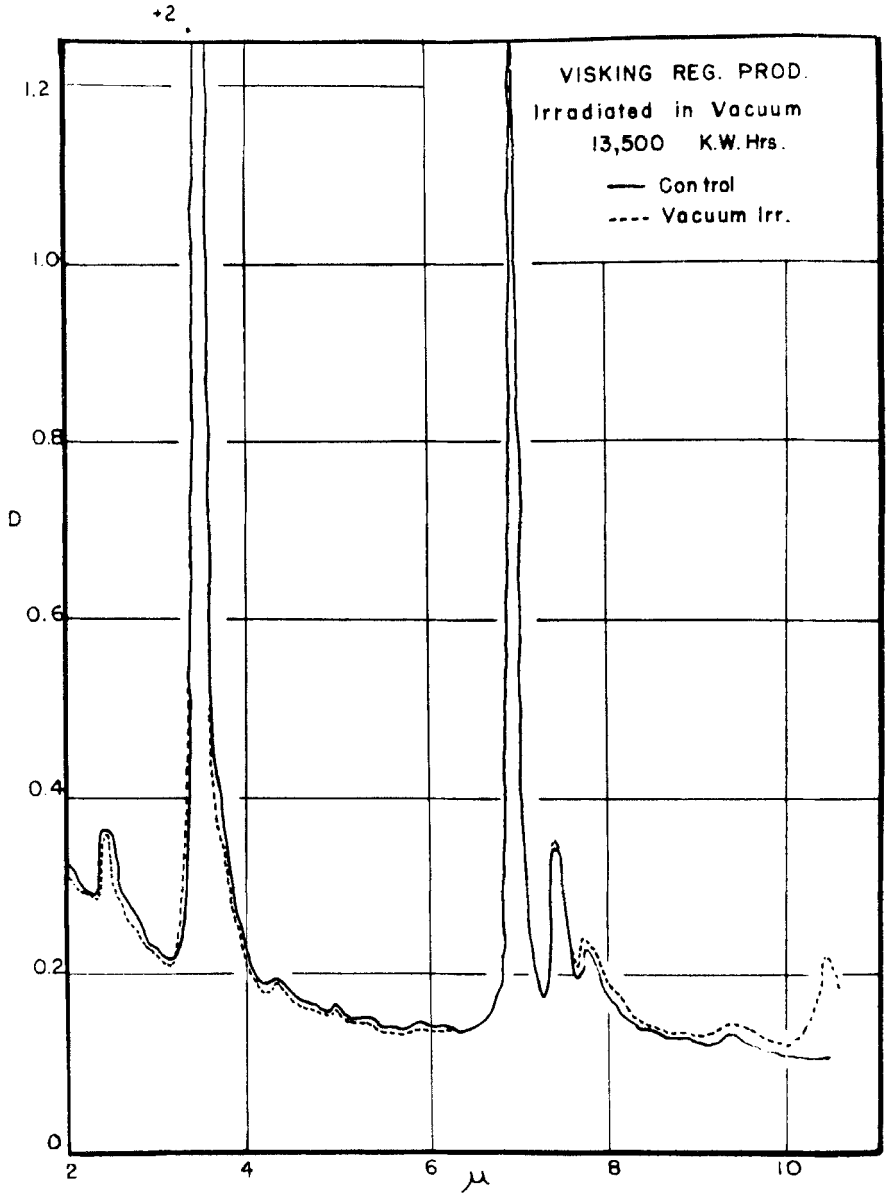

FIG. 3. Infrared absorption spectrum of polyethylene film before (solid line) and after (dotted line) an irradiation in vacuum.

Space does not permit an extended description of the mechanisms involved in the formation of cross-links by γ-ray or electron irradiation; suffice it to say that the radiation causes the evolution of hydrogen gas, and the breaking of the C–H bonds in the solid leaves behind mostly alkyl-type free radicals, $-CH_2\dot{C}HCH_2-$, which then migrate through the amorphous regions of the solid until free radicals on adjacent chains recombine to form the C–C covalent bond cross-links. As discovered by us in 1962 [9], molecular hydrogen markedly catalyzes the decay of the alkyl radicals in irradiated PE, and as the hydrogen dissolves only in the amorphous regions, the cross-link formation by the free radical decay reactions must occur in the amorphous phase or at the boundary between the crystalline and amorphous phases.

In conclusion, we wish to express our grateful appreciation of financial aid received for our radiation studies over these many years from the above-mentioned sources and from the U.S. Atomic Energy Commission, the Energy Research and Development Administration, the U.S. Department of Energy, and from income from the Chair in Chemistry endowed at Baylor University by The Robert A. Welch Foundation.

REFERENCES

[1] A. Charlesby, Nucleonics, 12(6), 20 (1954).
[2] L. M. Currie, U.S. Patents 2,027,961 and 2,027,962 (1936).
[3] Chemical and Engineering News, 26, 2289 (1948).
[4] M. Dole, "Effect of Radiation on Colloidal and High Polymeric Substances," in Report of Symposium IV, Chemistry and Physics of Radiation Dosimetry. Part 1–Unclassified Papers, Technical Command, Army Chemical Center, Maryland, September 1950, Paper 7, pp. 120-147.
[5] A. Charlesby, Proc. R. Soc. (London), 215A, 187 (1952).
[6] E. J. Lawton, A. M. Bueche, and J. S. Balwit, Nature, 172, 76 (1953).
[7] J. Silverman, Radiat. Phys. Chem., 14, 17 (1979).
[8] J. D. Hunt and G. Alliger, Ibid., 14, 39 (1979).
[9] F. Cracco, A. J. Arvia, and M. Dole, J. Chem. Phys., 37, 2449 (1962); see also M. Dole, J. Salik, and N. Gvozdic, Fundam. Res. Homogeneous Catal., 3, 83 (1979).