THE PHYSICS OF HIGH POLYMERS

A review of the field of high-polymer physics and of the Division of the American Physical Society which was founded in 1944 to represent that branch of physics.

. . . . *a survey and forecast*

By ***W. F. Busse***

MANY of the great physicists of the 19th Century were more familiar with today's problems of high-polymer physics than were those of the early 20th Century. Maxwell, Boltzmann, Joule, and others were interested in many problems in this field. Most of these problems were later forgotten or ignored in favor of the more exciting, fashionable, and important problems of x-rays, quantum theory, wave mechanics, and atomic structure, which have almost monopolized the attention of modern physicists.

With all this concentration on "modern" physics, there were still some surprising gaps in our knowledge of the physics of ordinary materials which persisted into the second quarter of the 20th Century. In 1925 we still had no good theory of the viscosity of liquids which could even predict the right sign for the temperature coefficient of viscosity.

Maxwell in the late 1800's had explained the small increase in the viscosity of gases on raising the temperature and Sutherland, Chapman, and others had refined this theory, but no one had even come close to applying it to liquids. It was not until after 1930 that Andrade, Eyring, and others made a start towards a reasonable theory of the viscosity of liquids.

The phenomenon of long-range elasticity was another effect that was bypassed by the main stream of physics. The effect is illustrated whenever we stretch a rubber band and let it snap back by releasing it. This experiment was probably first done by the Indians long before Columbus discovered America—but in 1930 we still had no theory to explain why the band retracted.

W. F. Busse, a former chairman of the American Physical Society's High Polymer Physics Division (1946), gave the talk upon which this article is based at the Detroit meeting of the APS in March 1954, the occasion of the Division's 10th anniversary. Dr. Busse is a member of the Polychemicals Department, Du Pont Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

Joule had studied the phenomenon and made the critical observation that the rubber became warm on stretching and cooled on retracting. This was contrary to the behavior of metals and was an unexplained phenomenon for many years. Standinger showed in the late 1920's that rubber consisted of giant "macromolecules" having some thousands of atoms held together by primary valences in a long chain. It was then possible to analyze the experiment of stretching the rubber band to deduce the necessary and sufficient conditions for high elasticity.

About 1932 it was recognized that the macromolecules are normally in a random kinky shape, due to thermal vibrations of the chain segments. Stretching rubber then changes the shape to a less probable arrangement, or one of lower entropy. The retraction of the stretched rubber then is due to the tendency of the Universe to increase its entropy to a maximum.

ANOTHER group of phenomena which were neglected included creep and stress relaxation. These involve the slow changes of length or stress which follow the initial elastic deformation when a load is applied to many types of material objects. Kolthoff demonstrated that if the loads on a sample were changed in a particular way the unloaded sample might first stretch and then contract during the recovery. Boltzmann explained these results by assuming that the effects of any given load are imposed on the effects remaining from every previous load throughout the history of the sample. While this Superposition Principle is elegantly simple and powerful, it is valid only provided there is a linear relation between stresses and strains.

Maxwell studied these effects and explained them by his simple model of a spring and dashpot connected in series. When this model did not fit observed data, an infinite series of such structures was postulated, giving

a whole spectrum of relaxation times. This gave enough degrees of freedom to match almost any data for creep under a constant load. However, the assumption of springs and dashpots was highly artificial and a much better and more realistic model was (and still is) needed.

After the First World War, there was an enormous increase in the study of the chemistry of high polymers and men began to turn out man-made fibers, elastomers, and plastics in a constantly increasing stream. In a few places, the physics of these materials was also investigated because it was realized that while man or nature made high polymers by chemical processes, the consumer purchased and used them primarily for their physical properties.

Work on the physics of polymers was active in this country at the Bureau of Standards, some universities, and a number of industries—particularly the rubber and plastics industries. In England there were also a number of laboratories studying the physics of rubber and of cotton.

At this time, the physicist studying polymers was something of a forgotten man. Occasionally papers on the stretching of rubber or the properties of textile fibers appeared on the Physical Society programs but they were lost in the flood of papers on spectroscopy and quantum theory that were coming out at that time. There was a need for some organization to bring together people who were interested in this field, and to stimulate discussions of the theoretical as well as experimental problems. The American Physical Society was aware of this situation and of similar problems in other fields of physics. The American Institute of Physics was organized to meet a part of this need. The American Physical Society also made provision in its charter for the establishment of separate divisions. A Division of Electron and Ion Optics was the first to be formed under this provision and there are now four Divisions in the Physical Society.

ONE effort of the Physical Society to meet the needs of physicists in the industrial fields was to organize a number of Symposia. One was held on Industrial Physics in Pittsburgh in 1940. Another was held on the Physics of Rubber in Evanston in 1943. This meeting attracted a large section of those people interested in high-polymer physics. The group was asked to vote on the question of whether they would prefer to have occasional Symposia or would rather have a separate Division within the Physical Society which would organize meetings at least once a year. About 95 percent of the audience voted in favor of establishing a separate Division to cover the physics of high polymers.

As a result of this vote, a committee consisting of P. Debye, J. H. Dillon, W. J. Lyons, L. A. Wood, and W. F. Busse was formed to petition the Council to organize a Division of High Polymer Physics. Later, Council President A. W. Hull appointed the above people, together with K. K. Darrow as chairman, to act as the Organizing Committee, and to work out the bylaws of the Division. Subsequently R. B. Barnes, F. G. Brickwedde, G. B. Pegram, and A. E. Ruark were added.

The inaugural meeting was held in Rochester in June, 1944. The executive committee, appointed by the American Physical Society, consisted of R. B. Barnes, W. F. Busse, P. Debye, J. H. Dillon, J. P. Elting, W. J. Lyons, and L. A. Wood. They elected J. H. Dillon, chairman; P. Debye, vice-chairman; and L. A. Wood, treasurer. Their choice for secretary was W. J. Lyons. He was liked so well that it has become a habit to elect him to this job, and he has served continuously ever since. In this feature, the Division of High Polymer Physics carefully followed the precedent of the Physical Society. When they found a good secretary, they kept him. In fact, since 1950 they made him both secretary and treasurer.

The next chairman was W. F. Busse. Then H. A. Robinson became chairman, and he probably did more work with his office than did any other chairman. This was because he arranged to edit and publish in book form the papers presented at the New York meeting in January 1947. The next chairman was L. A. Wood, who has also worked hard and long for the Division, and whose files were invaluable in furnishing data for this paper. Following him came: J. W. Liska, W. L. Davidson, J. B. Nichols, M. L. Huggins, and R. F. Boyer, under whom the excellent program of this Detroit meeting was prepared. J. D. Ferry, who is doing such good work on viscoelasticity at Wisconsin, is the new chairman.

We could go into great detail about the number of members and the number of papers presented at our Division, but perhaps it is enough to say that a rough calculation shows our batting average to be about the same as that of the Society as a whole.

MORE important than our history is our future. What new developments lie before us in the years ahead? We can expect to see the mechanical as well as the electrical properties of polymers studied over a very wide range of conditions—at frequencies from thousands of megacycles/sec to cycles/year, at deformation rates from kilometers/sec to microns/sec, and at temperatures from the melting range to close to absolute zero. The results will be interpreted first in terms of the spectra of relaxation times. These spectra will help us to understand the mechanical properties of these polymers—not only stiffness, but possibly also things like elongation, fracture, and the temperature coefficients of these properties. The relaxation spectra will also be interpreted in terms of model structures which are more realistic than the springs and dashpots of Maxwell's model.

When this is done, physicists will be in a strategic position to suggest molecular structures of polymers to be synthesized by the chemists to get the properties needed by the engineers to make better and cheaper products for better living.