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MASTER

PROGRESS REPORT

June 15, 1981 - Feb. 1, 1982

DEPARTMENT OF ENERGY
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Progress Report

DE-AT06-81ER10912

I. INTRODUCTION

The proposal entitled "Rubber Elasticity," submitted to the Department of Energy in August, 1980, and funded for the period from June 15, 1981 to June 14, 1982, described two projects to be conducted during a two year period. The first of these is an experimental study of the swelling of elastomers by diluents, and the second concerns theoretical analysis of the dynamics and thermodynamics of random networks.

New experimental results obtained during the first six months of the contract have an impact on our understanding of rubber elasticity that is just beginning to be felt. Approximations that have stood in this field for nearly 40 years are now discarded, and we are forced to reach for a new understanding of the behavior of elastomers.

Theoretical work on amorphous systems has thus far centered on evaluation of the density of states for models (constructed by others) of amorphous silicon, As_2O_3 , etc. We are currently assessing the utility of these models: although they have been used by solid state physicists to calculate properties of amorphous media, they suffer from the decided difficulty that there is no way to generate statistical averages from them.

A third project, not included in the original proposal, has also been conducted on this contract. We are synthesizing elastomers with metal-chelate crosslinkages. These materials will be useful in applications, and they promise to provide a host of new insights into the details of the physics of elastomers.

2. DIFFERENTIAL SWELLING

The experiments conducted during the first 6 months of this contract yielded results on five elastomer-solvent systems. The first system of this series was studied prior to June 15, 1981, but publication of a paper on those results was assisted by the contract. A second paper will appear in *Macromolecules* early in 1982, and a third is in preparation. In all cases polydimethylsiloxane samples, obtained from Prof. J. E. Mark of the University of Cincinnati, were used, and the systems investigated are summarized in Table I. This data allows comparison of (i) bulk and solution radiation-cured elastomers swollen with the same solvent (cyclohexane), (ii) one bulk radiation-cured elastomer swollen with two different solvents (cyclohexane and benzene), (iii) end-linked elastomers with constant chain length but with different junction functionality (three and four), and (iv) end-linked elastomers with a fixed junction functionality of four but with different chain lengths (DP 152 and DP 250).

The comparison (i) established the general validity of Flory's new constrained junction theory. During this work we found that a revision of the theory was required, and this has (at least partially) stimulated Flory to produce a modified version of the theory. The comparison (ii) definitely disproves the Flory-Rehner assumption that mixing and elastic free energies are separable. Research intended to encompass this finding will be described in the proposal for the next year. Comparisons (iii) and (iv) have not yet been made in detail; we are currently analyzing these data with Flory's latest theory in the hope that some regularity of the variation in parameters with chain length and junction functionality will become apparent. Stress-strain isotherms measured by Prof. Mark will be encompassed in the analysis. We expect to have this work completed by June of 1982. This research was done by Richard Brotzman, who completed his Ph.D. in December, 1981.

3. DENSITY OF STATES FOR AMORPHOUS MEDIA

Several models of amorphous semiconductors and insulating glasses have been constructed by others (primarily physicists) over the past 15 years or so. We were fortunate to obtain molecular coordinates and connectivity tables for several of these models from Prof. David Beeman of Harvey Mudd College. Calculations of the spectra of Kirchhoff matrices for the various models were carried out on the Vax computer in the Department of Chemistry by Neal Neuburger (Research Assistant). This research came to a rather abrupt halt when it became apparent that it is impossible to compare different models constructed by different people of what is ostensibly the same material (most notably amorphous Si). Statistical fluctuations from one model to another are sufficiently large to negate any meaningful analysis of trends with, say, the number of atoms contained in them. It is doubtful that much faith can be placed in the calculations of various properties of these models that have been carried out by others. It is absolutely mandatory that averages over an ensemble be computed for simulations like these. But since it is not an easy task to design algorithms to build random systems with narrowly constrained bond lengths and bond angles, the required ensemble averages have been inaccessible to all who have worked in this field.

A senior scientist from Hong Kong will be joining our group in April of 1982, according to present plans. We will then resume simulations on random systems, but our attention will be redirected to models of elastomers, for which statistical averages are attainable. We have algorithms at hand for the construction of models that will lead to improved realism in the results.

Much of the Principal Investigator's time during the summer months was spent in a literature search on amorphous systems. This is soon to culminate

in a review article on the density of states in amorphous media, which is to be co-authored with Dr. Brendan McKay, presently in the Department of Computer Science at Vanderbilt University. McKay's part of the article will center on the mathematical techniques of graph theory which are useful for this problem, and my part will be a comparison of what is known about the electronic states of amorphous semiconductors, the low temperature anomalies of glasses, the relaxations in simulated spin glasses, and the dynamics of elastomers. We have a commitment of interest from the Editors of Reviews of Modern Physics for this paper, and hope to have it ready for submission to them within a few months.

4. SYNTHESIS OF METAL-COMPLEX CROSSLINKED ELASTOMERS

The usual crosslinkages in elastomers are difficult to "see" in any physical or chemical experiment, yet the elastic modulus is critically dependent upon the number of crosslinkages. Researchers have generally been forced to resort to some physical measurement, such as the swelling equilibrium described in Part 2 above, to get information about crosslink density. As has been seen, these methods rely on theoretical approximations of dubious merit. Thus, it is imperative to obtain a direct chemical determination of crosslink density to compare with the physically measured number, so as to assess the validity of the several theoretical developments that have occurred in this area in recent years. We have the means to do this by synthesizing polymers with chelating functions pendant on the chains. These can then be bonded together through a metal ion to yield neutral complexes of very high stability. The metal atoms provide a convenient chemical marker, which can be inspected by a wide range of analytical and physical techniques.

A manuscript describing the polymers that Horng-Chin Yeh (PhD: March 1981) synthesized has been submitted to J. Polymer Sci. This work is currently being

extended by Nancy Iwamoto (Research Assistant), who is now preparing a large batch of styrene-isoprene elastomer for transmittal to Dr. J. E. Mark (Cincinnati) for stress-strain measurements and to Dr. Charles Han (NBS) for X-ray scattering. A preliminary sample was sent to Dr. Han, who found a Bragg peak at a location corresponding nicely with the known average distance between crosslinkages. Further experiments to be described in the proposal should yield excellent information on the deformation of the radial distribution function of junctions with strain and with swelling ratio.

We are also trying to terminate PDMS with acetylacetone functions, so as to produce an end-linkable system. The chemistry here is quite delicate, but we have achieved ca. 60% termination. We believe that with refinements this yield can be pushed far closer to 100%. When this succeeds we will have an elastomeric system that can be characterized in greater detail than has been achieved heretofore.

5. CONCLUSION

Our research program is aimed at a broad range of fundamental problems in elasticity. We are most interested in making rigorous experimental tests of theory and in advancing theory to give a deeper insight into the relationship between random network topology and physical properties. The experimental and theoretical results that have been obtained since the start of this contract have been significant to these ends, and this work will be continued in an effort to better understand this important class of materials. Elastomers are used as hoses and seals in harsh environments; an understanding of their capacity to imbibe diluents can lead to better designed materials. Random networks, such as those constituting elastomers, amorphous semiconductors, glasses, or nervous systems, deserve to be studied more than they have been

to date. At the very least we are breaking new ground and stimulating work in this area. A combination of mathematical analysis and computer simulation is enlightening this previously little explored field at a rapid rate.

TABLE I
Systems Studied by Differential Sorption
Polydimethylsiloxane Elastomers

Sample	Cure Type	Solvent	$v_{2,eq}^*$	$v_{2,max}^+$
1	Radiation, Soln	c-C ₆ H ₁₂	0.159	0.74
2	Radiation, Bulk	c-C ₆ H ₁₂	0.156	0.84
2	Radiation, Bulk	C ₆ H ₆	0.242	0.70
3	End-Linked	c-C ₆ H ₁₂	0.219	0.65
4	End-Linked	c-C ₆ H ₁₂	0.223	0.68
5	End-Linked	c-C ₆ H ₁₂	0.146	0.72

* Volume fraction of polymer at swelling equilibrium.

+ Volume fraction of polymer at maximum in the swelling function.

Description of Samples:

- 1: Radiation cured in 48% solution with γ -radiation from ⁶⁰Co source. The polymer contained 0.5 mole % (methylvinyl) siloxane units, and its molecular weight was 5×10^5 .
2. Radiation cured as 1, but in the undiluted state. This sample was selected from among many as having its swelling equilibrium near that for sample 1. The same sample was used with two different solvents.
- 3: Hydroxyl terminated PDMS of MW 11300 (narrow distribution) crosslinked with trialkoxysiloxane.
- 4: Same as 3, but crosslinked with tetraalkoxysiloxane.
- 5: Same as 4, but MW = 18500.

PUBLICATIONS and ABSTRACTS

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