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Polymer Gels as Precursors to High-Performance Materials

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11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION/AVAILABILITY STATEMENT

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13. ABSTRACT (Maximum 200 words)

The three types of materials covered in this investigation were (i) thermoreversible gels of organic polymers (such as polyethylene), (ii) non-reversible gels obtained by the hydrolysis of organometallics and used as precursors to inorganic ceramics (silica and titania), and (iii) hybrid composites prepared by having siloxane polymers present during the in-situ generation of the ceramic species. The kinetics of the gelation process were determined by measuring the shear moduli of the gels as a function of time for various compositions and catalyst concentrations. Of particular interest was the observed decreases in gelation time with increase in concentration of either catalyst (through increase in reaction rates) or polymer (through increases in the number of high molecular weight species necessary for gelation). Composites obtained by densification of the gels were characterized by NMR imaging, neutron and x-ray scattering, and impact strength measurements. The polymer components in the hybrid organic-inorganic composites was found to greatly increase their impact strengths.

14. SUBJECT TERMS

Gels, gelation kinetics, polymer-modified ceramics, composites, silica, titania, polysiloxanes, polyethylene, NMR imaging, shear modulus, impact strength

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Final Report

J. E. Mark

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1. FOREWORD

Optional; not included.

2. TABLE OF CONTENTS

Optional; not included.

3. LIST OF APPENDICES ...

Optional; not included.

4. BODY OF REPORT

A. Statement of Problem Studied

The primary goal of this project was to characterize the synthesis and structure of gels and their subsequent processing (aging, drying, densification, etc.) using both equilibrium and kinetic measurements. The types of gels included were thermoreversible gels of organic polymers, non-reversible gels obtained by the hydrolysis of organometallics to ceramics, and hybrid composite gels consisting of siloxane polymers bonded to the ceramic phases. The characterization techniques included neutron and x-ray scattering, NMR imaging, and impact strength measurements.

B. Summary of the Most Important Results

References are to the chronological list of publications given in the following Section (4. C).

Some gelation work was carried out to characterize the polyethylene gels of the type used for drawing ultrastrong fibers, using stress-strain isotherms obtained near elastic equilibrium.³ Of particular interest in this

regard were the "linear low density" polymers, in which hexene-1 is copolymerized with ethylene to provide a known number of branches, of known length. Even small numbers of the resulting butyl branches were found to have a significant effect on their gelation properties, in a way consistent with the changes they bring about in the resulting polymeric materials in the bulk state. This is providing guidance on optimizing conditions for preparing these ultrastrong fibers from the gel state.

The kinetics of the gelation process were determined by measuring the shear moduli of the ceramic-type gels.^{1,7,8} Typical hydrolysis reactions used to prepare them are shown by the equations



where the volatile alcohol is easily removed during the densification process. The moduli were measured as a function of time, for various compositions and catalyst concentrations. Once sufficient branching has occurred for gelation, the modulus begins to develop, increasing in an "S-shaped" manner, and then finally leveling off at its equilibrium value. The change in modulus with time, dG/dt , was interpreted using the equation

$$dG/dt = k [\text{EtOH/TEOS}]^x [\text{H}_2\text{O/TEOS}]^y [\text{NH}_3/\text{TEOS}]^z \quad (3)$$

where TEOS is the organometallic (tetraethoxysilane) being hydrolyzed, the ammonia is the catalyst, and x , y , and z characterize the order of the reaction. Of particular interest was the observed decrease in gelation time

with increase in concentration of catalyst (through increase in reaction rates). By general application of this approach, the order of the reaction could be determined with regard to each of the reactants, as well as with regard to the catalyst.

Of particular interest were the hybrid gels containing poly(dimethylsiloxane) as an organic phase, since these are used in the preparation of organic-inorganic composites. In this case, there was observed an additional decrease in gelation time with increase in concentration of polymer (through increase in the number of high molecular weight species necessary for gelation).

Another type of gel of interest were those used to prepare polymeric foams from polymer solutions that had been gelled by thermally-induced phase separations.⁵ It was possible to correlate their mechanical properties with the conditions used in their preparation.

The composites obtained by densification of the gels were characterized by neutron and x-ray scattering, ¹H NMR imaging, and impact strength measurements.^{1,7,8} [The small angle x-ray scattering (SAXS) work was done at either the Oak Ridge National Laboratories or the University of Cincinnati, and the small angle neutron scattering (SANS) work was done either at Oak Ridge, or the Los Alamos National Laboratories. This part of the research was done in collaboration with Dr. Dale W. Schaefer of Sandia National Laboratories, and Professor Keith Keefer of the University of Cincinnati.] These scattering results were used to categorize the materials into particulate and non-particulate dispersions, and into systems that had either continuous polymer phases, continuous ceramic phases, and interpenetrating bicontinuous phases.

The NMR imaging results were used as a non-invasive, non-destructive technique for determining the polymer distribution in silica aerogels that had been impregnated with poly(dimethylsiloxane) to form a novel type of composite.²

The mechanical property measurements^{4,6} on the densified composites showed that the ceramic components present in the polymer matrices greatly increased their moduli and toughness, and the polymer components present in the ceramic matrices greatly increased their impact strengths.

Scattering studies were also carried out on some elastomeric materials which had been reinforced by blending zeolites into them.⁷ Previous investigations of the mechanical properties of these materials showed that the reinforcement was much better when the zeolite employed had a relatively large cavity (10 Å) rather than a small one (3 Å). It was attempting to speculate that the former had better reinforcing ability because its cavities were large enough to be penetrated by the elastomeric polymer chains. The neutron scattering results indicated that the chains did not thread through the zeolite cavities in the approach taken. This suggests that the mechanical properties of this type of composite could be improved even more by having monomer present in the cavities of the zeolite, and then polymerizing it to give a organic-inorganic composite in which the two phases are certain to be intimately interspersed.

C. List of All Publications and Technical Reports

1. Some Novel Polysiloxane Elastomers and Inorganic-Organic Composites, J. E. Mark, J. Inorg. Organomet. Polym., **1**, 431 (1991).
2. Polymer Distribution in Silica Aerogels Impregnated with Siloxanes by ^1H NMR Imaging, L. Garrido, J. E. Mark, S. Wang, J. L. Ackerman, and J. M. Vevea, Polymer, **33**, 1826 (1992).
3. The Use of Mechanical Property Measurements to Characterize Gels and Gelation Processes, Y. Yang, N. Ichise, Z. Li, Q. Yuan, J. E. Mark, E. K. M. Chan, R. G. Alamo, and L. Mandelkern, in "Complex Fluids", ed. by E. B. Sirota, D. Weitz, T. Witten, and J. Israelachvili, Materials Research Society, Vol. 248, Pittsburgh, 1992.
4. Reinforcement from In-Situ Precipitated Silica in Polysiloxane Elastomers under Various Types of Deformation, J. E. Mark, S. Wang, P. Xu, and J. Wen, in "Submicron Multiphase Materials", ed. by R. H. Baney, L. R. Gilliom, S.-I. Hirano, and H. K. Schmidt, Materials Research Society, Vol. 274, Pittsburgh, PA, 1992.
5. The Elastic and Plastic Mechanical Responses of Microcellular Foams, M. H. Ozkul, J. E. Mark, and J. H. Aubert, J. Appl. Polym. Sci., **48**, 767 (1993).
6. Synthesis and Properties of Inorganic/Organic Hybrid Materials Prepared by the Sol-Gel Process, J. Wen and J. E. Mark, submitted to Preprints, ACS Div. Polym. Mats. Sci. Eng., Chicago, August, 1993.

7. Organic-Inorganic Composites, J. E. Mark, submitted to "Frontiers of Polymers and Advanced Composites", ed. by P. N. Prasad, Plenum, New York.

8. Biomimetic, Hybrid, and In-Situ Composites, J. E. Mark and P. D. Calvert, submitted to Mats. Sci. Eng. C: Biomim. Mats.. Sens.. Syst.

D. List of All Participating Scientific Personnel

1. Professor James E. Mark, Principal Investigator
2. Professor Burak Erman, Visiting Scientist
3. Dr. Shuhong Wang, Graduate Student, Ph. D. Degree received 1991
4. Dr. Ping Xu, Graduate Student, Ph. D. Degree received 1991
5. Dr. Yong Yang, Graduate Student, Ph. D. Degree received 1993
6. Mr. Jonathon Breiner, Graduate Student
7. Ms. Qingwen Yuan, Graduate Student
8. Mr. Naoji Ichise, Graduate Student
9. Mr. Jianye Wen, Graduate Student

5. REPORT OF INVENTIONS

None obtained.

6. BIBLIOGRAPHY

Same as Part 4.C.