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Introduction

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Symposium on Polymers in Space Research: Part II, Properties of Polymers at Low Temperatures

Introduction

The second day of the Symposium on Polymers Research was devoted to the topic of "Properties of Polymers at Low Temperatures." It was divided into two sessions: one on fundamentals and the other on applications. The former was chaired by M. Shen, the latter by W. D. English.

The study of the behavior of polymers at low temperatures is motivated, on the one hand, by the desire to learn more about the nature of polymers in the glassy state and on the other by their applications as structural materials for cryogenic systems, of which space exploration is one of the most glamorous. Activities in this field during the past decade and a half have garnered a wealth of information. Scientifically, this information has permitted us to gain at least qualitative insight into the molecular dynamics that underlies the observed behavior. Initially, 77°K (the temperature of boiling liquid nitrogen) was the lower temperature limit of most of these studies. More recently there has been increased interest in extending the investigation to liquid helium temperatures (4°K) and below. This is the area of concentration for most papers given in this part of the symposium.

The session on fundamentals consisted of four papers. The first two papers in this session reviewed the recent advances in this field. Thus Sauer and Saba showed the effects of various internal and external variables that affect the low-temperature relaxation processes. Data from mechanical, dielectric, as well as nuclear magnetic resonance studies, were brought together to indicate the molecular mechanisms for these relaxations. Reese, on the other hand, scrutinized the thermal behavior of polymers at very low temperatures. The interesting feature of this work is the interpretation of these data in terms of theories from solid-state physics. The attempt represents another commendable step toward the potentially fruitful linkage between solid-state and polymer physics.

The other two papers were original research contributions. Schell, Simha, and Aklonis studied the low-temperature relaxations in polyvinyl alkyl ethers by both linear thermal expansion and torsion pendulum measurements. It was here demonstrated that the amount of "frozen-in" free volume at the glass transition temperature is not a universal constant but depends on the number of sub-T_g relaxations. Shen, Strong, and Schlein

investigated the effect of diluents on the internal friction of polymers at very low temperatures. The presence of diluent molecules was found to exert an "antiplasticization" effect on the low-temperature relaxations.

The four papers presented in the afternoon session were concerned with the applications of polymers in low-temperature environments. Current emphasis on composite structures was very noticeable, since three of the four papers dealt with adhesion by polymers at cryogenic temperatures. The primary direction was toward macrocomposites, not resins, but the lessons from the one area should be transferable to the other.

The paper by Tiezzi and Doyle dealt with the development of test methods to determine the mechanical stress, strain, and modulus properties of adhesives at cryogenic temperatures and the subsequent evaluation of a typical polyurethane adhesive. Robbins, again using polyurethane as a model adhesive, developed test methods based on rebound resilience, tensile properties, and cryogenic differential thermal analysis (DTA). The urethane had T_g of 243°K. Resilience minima occurred at 270 and 180°K and in the unexpectedly low range of 80-150°K. Tensile tests showed elongations of up to 200% at 195°K, 5% at 76°K, and brittle behavior at 4°K. Gosnell and Levine reported on a study of the relation between cryogenic adhesive properties and the polymer structure. Hydrogen bonding and internal flexibility were shown to be important parameters. A pure peel test was found to be the best method of evaluation, superior to lap shear. The most surprising finding was that polybenzimidazoles, with a very high T_g (above 700°F), were among the most effective cryogenic polymers. A hypothesis based on "frozen-in" energy and secondary relaxations was presented as a possible explanation.

The fourth paper, by Toy, English, Crane, and Toy, dealt with the chemical compatibility at cryogenic temperatures of nitroso rubber, a polymer developed as a flexible bladder material for rocket propellants. This is a relatively neglected area of vital importance to rocket vehicles.

As a closing note, it should be mentioned that the new areas of application for polymers which retain their performance at cryogenic temperatures are not limited to space. Superconducting magnets, superconductivity particle accelerators, apparatus for cryosurgery and cryobiology, and the ground-based antenna elements for satellite communications systems are just a few of the rapidly developing advanced technologies which use some, and will use many more, polymer materials. Because of such requirements,

the study of low-temperature properties of polymers will be a lively field of research in the years to come.

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