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DEFORMATION OF POLYMERS

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FINAL REPORT
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U. S. ARMY RESEARCH OFFICE - DURHAM

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13. ABSTRACT

The deformation of linear polymers was investigated from three viewpoints: 1) the microscopic, involved measurements of free volume and the relationship of the intermolecular forces to the yield point, 2) the phenomenological, involved the prediction of non-linear viscoelastic programs of deformation in terms of the creep curves, and 3) environmental crazing at low temperatures, involved the effects of gases on the tensile deformation. Experiments and theories concerning these three viewpoints are presented.

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I. Introduction

As one reads this report it will be immediately evident that there is nothing about oriented polymers as such and, thus, the research does not seem to have much relationship to the title of the original proposal "Deformation of Oriented Polymers." The general objective was to determine how polymers fail by yielding and it was originally thought that oriented polymers would offer a special insight into the deformation behavior of all linear polymers both oriented and unoriented. The research was initiated with oriented polymers, but it appeared that orientation was one but not the primary variable whereby the yield behavior of polymers might be understood.

The research advanced in several directions each of which took a different view of yielding. Consequently the report is divided into three parts or approaches. These approaches contain ideas and new observations which impinge on the frontier between our knowledge and ignorance of the deformation of polymers. Part A of the body of the report deals with fundamental questions of how the molecular state governs the yield point. The role of free volume, viscous effects, and defects were considered. Part B describes a phenomenological approach for understanding non-linear visco-elastic behavior in polymers in order to predict when the polymer will fail under various loading conditions. The general goal is to determine how creep tests can be used to predict the deformation at high stresses and strains near the yield point for cyclic loading, constant strain rate tests, and stress relaxation. Part C describes how gases affect the tensile strength of all polymers at low temperatures by causing them to craze. This effect was discovered by Parrish and Brown who found that N_2 and Ar change the tensile strength at 78°K. Consequently all existing mechanical properties of polymers at cryogenic temperatures have to be given a fresh look in an inert environment in order to understand the intrinsic behavior of polymers at low temperatures. Each of the sections will be described briefly since publications or reports are available.

II. Body of Report

A. Statement of Problem

The general problem was to determine the mechanism whereby linear polymers yield and the factors that determine the yield strength. The research attempted to answer the following specific questions:

(a) What are the fundamental molecular processes that occur when a polymer yields and how do these processes determine the strength or yield point of the polymer?

(b) Is it possible to predict the yield failure of a polymer which is subjected to arbitrary loading if its creep behavior is known?

(c) What is the mechanism whereby gases such as nitrogen and argon cause polymers to craze or otherwise modify their strength at low temperatures?

Although the three questions are somewhat interrelated, this report will be divided correspondingly into three sections:

1. Fundamental Aspects
2. Predicting Failure for Arbitrary Loading
3. Environmental Crazing at Low Temperatures

B. Results

1. Fundamental Aspects

There are several viewpoints for describing the yielding of polymer. The free volume viewpoint states that as the stress increases the free volume, the polymer flows faster until it yields under a constant stress. There is the visco-elastic viewpoint that says polymers do not yield, but that they are like viscous fluids which will effectively flow or yield at an arbitrarily low stress if the strain rate is low enough. There have been attempts to correlate yielding with the notion of defects, like dislocations, whose stress controlled motion determines the yield point. There is the viewpoint that yield processes can be divided into craze yielding and shear yielding, depending on the stress field, and each of the types of yielding may occur by somewhat different molecular processes. This part of the research attempted to understand the role of free volume and viscous effects on shear yielding.

Compression tests were emphasized in order to avoid crazing and to determine how yielding occurs when the free volume is decreased by the stress. The change in volume of the specimens were measured during the stress-strain test up to the yield point. The results in compression for three polymers, polycarbonate, polytyrene, and polymethylmethacrylate were the same. The excess free volume of the polymers increases in compression and decreases in tension as the polymer begins to yield. The excess free volume is defined as the total change in volume of the polymer minus the elastic change in volume as obtained from the value of Poisson's ratio at zero strain. The results showed that Poisson's ratio started at about 0.35 for all polymers and then increased with strain to a value less than 0.50. The latter value denotes incompressibility.

The significance of the results is that during compression yielding there is a non-linear dilatational process and during tensile yielding there may be a non-linear contracile process. The non-linear dilatational part of the volume change, which was observed during compression, was found to be reversible in that there was practically no permanent volume change after the material had yielded. The conclusion from these experiments has been that although free volume changes during yielding and excess free volume tends to make yielding easier, the generation of a critical amount of free volume does not determine when yielding occurs. Yielding occurs whether or not there is an increase in free volume at the yield point.

The viscoelastic viewpoint has been examined. Creep data and data on time to failure versus stress indicate that polymers below T_g will not yield below a certain stress. Even at extremely small strain rates there is a limiting stress required for plastic deformation.

The dependence of yield point on Young's modulus and the fact that elastic strains of about 5% occur at the yield point, have led to the conclusion that shear yielding is related directly to the intermolecular forces. Calculations of the theoretical yield point based on a Van der Waals 6-12 potential indicate that the ratio of yield point to Young's modulus should be about 1/30 and the yield strain about 5%. The experimental data for polymers are in this range. Shear is the fundamental process and under tensile, compressive or shear stresses, molecular separation must occur in order that shear takes place. The critical separation at the yield point has been related to the intermolecular force. In summary, free volume, and strain rate modify the yield stress, but the basic value of the yield stress is determined by the average intermolecular forces rather than by some defect mechanism.

2. Predicting Failure under Arbitrary Loading

The goal is to predict the results of arbitrary loading in terms of the creep function. In the linear region this problem has been solved by the Bolzmann Superposition Principle. The problem is very far from being solved for high stress in the non-linear region of viscoelasticity. A start was made by correlating recovery with creep because recovery under zero stress is a very simple process and because combinations of creep and recovery can be used to duplicate more complex loading programs. It was found that recovery could be predicted from the creep data, at least in the case of polycarbonate, if the creep strain were in the recoverable region. It was also found that creep failure occurred at a critical strain.

The critical strain for creep failure was decomposed into an instantaneous elastic strain, a time dependent recoverable strain, and a persistent strain. The accumulation of the persistent strain was associated with creep failure.

Sequential creep and recovery experiments were performed in order to duplicate the cyclic loading that occurs during fatigue. The stress was varied between zero and a fixed compressive stress. The loaded or creep part of the cycle and the unloaded or recovery part of the cycle were varied. A general result was that a period of recovery decreased the time to creep failure for polycarbonate.

Measurements were made of the temperature changes that occurred during creep and recovery. It was found that the temperature changes were not the fundamental cause of creep failure. However, the temperature rise that occurred during deformation could hasten failure, but the temperature rise was not a necessary condition for failure.

These experiments indicate that the creep function at high stresses is the best basis for developing an understanding of shear deformation during other types of tests such as stress relaxation, constant strain rate, and cyclic loading. A complete solution is difficult because the phenomenon is non-linear and because the nature of the persistent strain that is responsible for failure is not understood. It is suggested that quantitative correlations between creep and the other types of loading programs will be more simple if all strains are limited to the reversible domain.

3. Environmental Crazing at Low Temperature

It was discovered by Parrish and Brown that nitrogen and argon affect the tensile yield and fracture behavior of all polymers in the vicinity of 78°K. This discovery means that all existing tensile yield data, which generally had been obtained in a H_2 environment, were influenced by the environment. Consequently the intrinsic low temperature tensile yield and fracture properties need to be determined in an inert atmosphere which may be either helium or vacuum. The most profound effects of the H_2 and Ar are to produce crazing and to cause the stress-strain behavior to be very strain rate dependent. It was one purpose of the research to understand the nature of this environmental effect.

The generality of the effect on all linear polymers, both amorphous and crystalline, and also on a cross-linked polymer was demonstrated.

A theory was developed which showed that the effect was related to the adsorption of gases on the surface of the polymer. The adsorption leads to a large percentage reduction in surface energy (25-75%) and to plasticization at the root of notches or the tip of a craze. The theory also explains that the environmental effect dies out above a certain temperature which is related to the desorption characteristics of the particular gas. The adsorption isotherms serve as the basic data for predicting the range of temperature and pressure where a particular gas and polymer will exhibit environmental crazing. As an example, the theory shows that for N_2 on PTFE the environmental effect on the tensile strength disappears above about $200^{\circ}K$ in agreement with experiments.

The relationship of the degree of crystallinity to the environmental effect was investigated in PTFE. It was found that in an inert atmosphere the least crystalline material was strongest at $78^{\circ}K$, but weaker at $200^{\circ}K$. However, the least crystalline material was strongest in both N_2 at $78^{\circ}K$ as well as in acetone at $200^{\circ}k$. Thus, the effect of crystallinity on tensile strength depends on both the temperature and the environment.

The influence of surface defects on environmental crazing was investigated. It was found that N_2 at low temperatures could blunt the defect and increase the fractures strength. The nitrogen could also enhance crazing in cooperation with the stress concentration produced by the defect. The blunting of the defect which strengthens the polymer occurs at high strain rates and the crazing effect which weakens the polymer occurs at low strain rates. This finding should be an important consideration in the study of fracture at low temperatures.

C. Conclusions

1. Fundamental Aspects

(a) It is concluded that the intrinsic shear strength of polymers is mostly determined by the stress necessary to overcome the average intermolecular forces between the molecules and that the strength is more closely related to the bulk properties of the polymer rather than to isolated defects.

(b) The important bulk property which best predicts the yield point of a polymer is Young's modulus knowing that the ratio of yield point to Young's modulus is generally in the range of 1/30 - 1/60.

(c) Free volume effects the yield point but it is not the basic parameter that determines yielding.

(d) The strain rate effects the yield point, but there is generally a critical stress below which yielding will not occur no matter how low the strain rate. The critical stress is governed by the average intermolecular forces.

2. Predicting Failure under Arbitrary Loading

(a) For predicting how polymers will deform by shear yielding under an arbitrary loading schedule, compression creep data are most useful

(b) The deformation can only be predicted if the strain is separated into its instantaneous, recoverable, and persistent components.

(c) The creep and recovery characteristics of a polymer are related to its behavior under cyclic loading.

(d) With polycarbonate, a period of unloading (recovery) makes the polymer fail faster in creep as compared to a continuous creep test.

(e) The temperature changes that occur during a creep test are not primarily responsible for creep failure.

3. Environmental Crazing at Low Temperature

(a) Nitrogen and argon effect the tensile strength of all polymers below about 200°K usually by inducing crazing.

(b) The tensile strength in N_2 or Ar may be greater or less than the tensile strength in the inert environments (He or vacuum) depending on the strain rate. Higher strain rates enhance the tensile strength in the active environment relative to that in the inert.

(c) The environmental effect is related to the reduction of surface energy caused by adsorption.

(d) The environmental effect disappears at higher temperatures because desorption occurs.

III. List of Publications and Reports

(a) "Creep and Recovery of Polycarbonate", Journal of Material Science, June 1973 by M. J. Mindel and N. Brown.

(b) "A Theory for Environmental Craze Yielding of Polymers at Low Temperatures," Journal of Polymer Science (in Press) by N. Brown.

(c) Journal of Applied Physics, October, 1973 by S. Fischer and N. Brown.

(d) "Deformation of Polymers in Compression," M.S. Thesis from Department of Metallurgy and Material Science, University of Pennsylvania (available by September, 1973) by Richard A. Lathlaen.

(e) The Relationship Between Creep, Recovery, and Cyclic Loading in polycarbonate, Technical Report (in preparation) by M. J. Mindel and N. Brown.

IV. Participating Scientific Personnel

Dr. Norman Brown

Dr. M. J. Mindel

Dr. M. F. Parrish

Mr. R. A. Lathlaen

Mr. S. Fischer

(Mr. Lathlaen will receive the M.S. degree in 1973.)