This report summarizes the results of a research program to bring polymer science and fracture mechanics technologies to bear on the subject of polymer fatigue. The first major thrust area concerned an analysis of fatigue fracture micromechanisms in amorphous engineering plastics.
Final Report

FATIGUE CRACK PROPAGATION
IN POLYMERIC MATERIALS

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Statement of the Problem Studied

The overall objective of the research conducted under ARO-D grant support was to combine a study of fatigue crack propagation (FCP) in polymeric materials using fracture mechanics concepts with a characterization of their molecular, morphological, and both linear and non-linear deformation behavior. To this end, an interdisciplinary research team, involving members from both the Polymer and Mechanical Behavior Laboratories of the Materials Research Center, was assembled to implement the program.

One phase of the research program was designed to study the effect of external test variables such as test frequency, temperature and waveform on fatigue fracture response in numerous polymeric solids. The purpose of this investigation was to determine what effect, if any, hysteretic heating had on the fatigue behavior of engineering plastics. Furthermore, the origin of FCP test frequency sensitivity was to be examined in terms of possible creep-fatigue superposition, strain rate dependence of tensile strength and elastic modulus and/or some type of resonance condition between test machine oscillation rate and molecular main chain or segmental motion jump frequency.

The micro-mechanisms associated with the fatigue fracture process were to be deduced with the aid of transmission and scanning electron microscope observations. Of prime interest was a comparison of fatigue fracture mechanisms observed in various matrix resins under different test conditions. Fatigue striation spacings were to be measured and compared at given $\Delta K$ levels with macroscopically determined crack extension rates. Furthermore, the micro-mechanisms associated with discontinuous crack growth were to be examined and a model proposed to explain the genesis of this cracking process. Also, it was necessary to determine the generality of this mechanism.
in the amorphous polymers other than PVC and in other materials such as rubber-modified and crystalline polymers.

Finally, the FCP response of selected polymeric solids was to be evaluated in terms of internal molecular structure and properties such as molecular weight and molecular weight distribution. Regarding the latter, it was desirable to determine whether FCP sensitivity to $M$ was a function of $M_n$, $M_w$, or $M_z$. Other studies were planned to examine the role of second phase additions in enhancing fatigue fracture resistance. Also, changes in FCP rates with internal and external plasticization, cross-linking.
Summary of Major Results

The major intent of this research program was to bring polymer science and fracture mechanics technologies to bear on the subject of polymer fatigue. We feel that this objective was clearly achieved as measured by a number of different criteria. First, the Lehigh blend of interdisciplinary research led to twenty-one joint publications spanning the five years of the grant. Four other papers are presently being drafted, bringing the total number of manuscripts to twenty-five. Second, our successful activities have received the attention of a major book publisher, Academic Press Book Co., who has contracted with us to publish a book dealing with the fatigue behavior of plastics. Third, our research efforts have prompted numerous invitations for us to present papers at both national and international meetings sponsored by the APS, ACS, AIChE, ASTM, SPE, the Plastics and Rubber Institute, and the International Union of Pure and Applied Chemistry in the United States, England, and France. In a related manner, John A. Manson was invited as guest lecturer to the Gordon Conference on Polymers (1978) to discuss ARO-D research findings and Richard W. Hertzberg was invited to deliver the important William Woodside Memorial Lecture at the Detroit Chapter of ASM and spoke on the subject of plastic fatigue.

Considerable progress was made in three principal subject areas and the results of these findings will be discussed separately. First, a major thrust area concerned an analysis of fatigue fracture micromechanisms in amorphous engineering plastics. In certain materials such as polystyrene, polycarbonate, poly(methyl methacrylate) and polysulfone, fatigue striations were found at relatively high stress intensity levels. The spacing between these bands—representing the increment of crack advance resulting from one local excursion—was found to be in excellent agreement with macroscopic
crack growth rate measurements and confirmed fracture surface observations to the extent that fatigue striations represented the only operative fatigue fracture micromechanism in this ΔK regime. At lower ΔK levels in these materials as well as in poly(vinyl chloride), ABS and polyacetal, the fracture surface revealed another set of parallel fracture markings. These bands have been identified as discontinuous growth bands whose width corresponds to the dimension of the plastic zone at the advancing crack front as computed from the Dugdale formulation. Video tape images have been used to verify that continuous craze growth occurs during periods where no crack extension is observed. The duration of the successive periods of crack dormancy between sudden bursts of crack extension range from as few as 15 loading cycles to as many as 100,000 cycles, depending upon the material and its structure and the magnitude of the stress intensity factor. It is concluded from this phase of the study that extreme care be exercised when examining the fracture surfaces of plastic components since fatigue fracture lines may represent a single load excursion or as many as 100,000 such load cycles.

A second subject area that received considerable attention during the grant period involved a study of the fatigue crack growth rate dependence on test frequency. Based upon previous polymer fatigue reports available in the open literature, concerning hysteretic heating effects, one would have expected that FCP rates would increase with increasing test frequency. And yet, this was not found to be the case. Instead, numerous polymeric solids exhibited FCP rates which actually decreased with increasing test frequency while other polymers showed no crack growth dependence on test frequency. After considerable experimentation and analysis, it was found that the fatigue crack growth dependence on test frequency was keyed to a
resonant condition between the oscillation rate of the test machine and the jump frequency associated with segmental motion corresponding to the damping peak. Whenever these two frequencies were of the same magnitude, FCP rates were found to decrease with increasing machine oscillation rate. Tests conducted at various temperatures confirmed our prediction that FCP frequency sensitivity could be enhanced or minimized by changing the ambient resonant condition (i.e., temperature) between machine and segmental motion oscillation rates. It has been argued that when resonance does occur, the resulting localized heating at the crack tip provides additional plastic flow that acts to blunt the crack tip, thereby slowing the advance of the crack front.

The third, and perhaps, major focus area has been directed toward an analysis of polymer chemistry and architectural effects on FCP. From our earlier studies, it became clear that the fatigue crack propagation resistance of numerous engineering plastics varied to a much larger degree than that predicted from companion studies of different metal alloy systems. Crystalline structures proved to be superior to amorphous polymers, rubber additions enhanced fatigue resistance, and cross-linking caused crack growth rates to increase. Overall, it was found that the $\Delta K$ level required to drive a crack at a specific growth rate increased with increasing material fracture toughness. The effect of internal and external plasticization on crack growth rates was studied in PMMA and PVC, respectively. No significant effect of the external plasticizer, dioctyl phthalate, on FCP rates was found on PVC while additions of butyl acrylate to PMMA produced major changes in fatigue behavior. We concluded from these studies that significant changes in polymeric fatigue response may be expected when basic changes are made to the character of the chains themselves.
The most significant observations with regard to this phase of the grant have dealt with the role of molecular weight and molecular weight distribution on fatigue crack propagation rates and the associated fracture micromechanisms. Though the modulus of elasticity, glass transition temperature and yield strength do not change appreciably with molecular weight above a certain level, fatigue crack growth rates in PVC were found to decrease by at least two orders of magnitude when $\bar{M}$ increased 3½-fold from 66,000 to 225,000. Similarly, a three decade decrease in FCP rates in PMMA accompanied a 50-fold increase in $\bar{M}$. Crack growth rates in these two materials were found to depend on $M$ with a relationship of the form $da/dn \propto \Delta K^{1/M}$. These studies also revealed that the discontinuous crack growth process occurred in polymeric solids only when $M$ was less than about 400,000. Both the fracture mechanism transition and the change in growth rates was related to the relative tendency for craze breakdown based on the concentration of long chain molecules within the craze zone.

Finally, it was confirmed that the presence of a small fraction of high-$M$ or low-$M$ chains exerted a large influence on FCP resistance even when $\bar{M}$ changed little. For example, FCP rates at a constant $\Delta K$ level were found to correlate best with the inverse of $M_z$. As the proportion of low-$M$ ($M < M_o$) in high $M$ matrixes were increased, FCP rates at constant $\Delta K$ increased in a regular fashion until catastrophic fracture intervened, at about 27 wt% low-$M$ material. When high-$M$ tails were present in low-$M$ matrixes, however, up to ~75% low-$M$ material could be tolerated before catastrophic fracture. Thus, it appears that for a given fraction of low $M$ component in a bimodel blend, the fatigue response depends upon the polymerization sequence. These results may be interpreted in terms of the relative ability to form stable entanglement networks.
Grant Publications

The five-year term of this grant was highlighted by considerable progress, resulting in the publication of twenty-one (21) scientific articles in various technical journals and conference proceedings. Four additional manuscripts are currently being drafted and should be submitted for publication by the end of this calendar year. Finally, the principal investigators are in the process of completing a monograph entitled "Fatigue Processes in Engineering Plastics" that is to be published in late-1979 by the Academic Press Book Company. The results from this ARO-D program will serve as a major focus in this treatise.

The list of publications which follows has been divided into three sub-sections to reflect the achievements made in three major research thrust areas described in the previous section. While a number of these papers deal with more than one or all three major subject areas, they are listed in only one sub-section. A fourth section is added to indicate the subject matter of the manuscripts currently being drafted.

John A. Mann

Richard W. Heftley
A. Material variables affecting FCP:


B. Frequency dependence of FCP:


C. Micromechanisms of FCP:


Manuscripts in Preparation


