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FATIGUE CRACK PROPAGATION IN CRYSTALLINE POLYMERS AND
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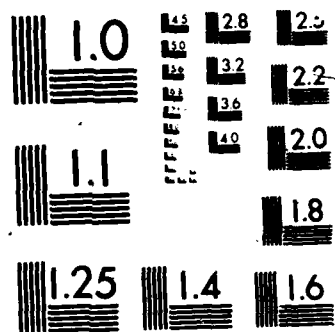
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FINAL REPORT

FATIGUE CRACK PROPAGATION IN
CRYSTALLINE POLYMERS AND COMPOSITES

OFFICE OF NAVAL RESEARCH

PROJECT NR356-670

CONTRACT NO. N00014-77-C-0633

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TASK NO. NR356-670

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SELECTED
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FUNDING HISTORY

SEP 1977 - AUG 1978,	\$51,561
SEP 1978 - AUG 1979,	\$50,000
SEP 1979 - JUNE 1981,	\$99,945
JULY 1981 - MAY 1982,	\$65,000
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JUNE 1983 - MAY 1984,	\$80,000
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DESCRIPTION OF PROJECT

As polymers are used to an increasing extent in load-bearing applications, often under cyclic or repetitive loads, an understanding of fatigue behavior is important. Since all polymers contain flaws that may, under appropriate conditions, develop into catastrophic cracks, the fatigue crack propagation (FCP) response is of particular interest to the engineer. The role of polymer structure and composition in the kinetics and energetics of FCP is, in turn, of fundamental chemical and physical concern.

Our understanding of this role of polymer chemistry in the mechanics of fracture has been greatly increased during the past decade. However, although crystalline polymers as a class exhibit superior resistance to FCP, attention has been concentrated on glassy, amorphous polymers which are simpler to study. This project was begun in order to advance our basic knowledge of FCP in crystalline polymers, and has been extended to other multiphase systems such as those containing fibrous or particulate phases.

The principal goal was to elucidate the role of polymer structure, composition, and morphology on the kinetics, energetics, and mechanisms of FCP in typical crystalline polymers, as well as the effects of external variables such as frequency and stress range. Emphasis was placed on the effects of molecular weight, percent crystallinity, morphology, and where appropriate, environment. With respect to reinforced polymers, the emphasis was on the role of fiber content, fiber orientation, interfacial adhesion, and matrix properties. In all



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cases, the characteristics of the process or damage zone at the crack tip was determined wherever possible.

This proposal was conducted jointly within the Polymer and Mechanical Behavior Laboratories of the Materials Research Center, and was conducted in parallel with a complementary project on fatigue in amorphous polymers sponsored by the National Science Foundation.

MAJOR ACCOMPLISHMENTS

Semi-crystalline Polymers

1. The role of crystallinity on FCP behavior of typical semi-crystalline polymers, including poly(vinylidene fluoride), polyacetal, nylon 66, nylon 610, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and polypropylene was determined as a function of ΔK , the range in stress intensity factor, and hence in the range of applied load. In general, such polymers as a group exhibited much greater resistance to fatigue than amorphous polymers. Thus, at a given value of ΔK , crack growth rates tended to be lower than with typical amorphous polymers, while the value of ΔK required to drive the crack at a given velocity was higher. It was concluded that deformation of the crystallites constitutes a beneficial energy sink that increases the driving force required for crack extension.

2. The micromorphology of fracture was thoroughly examined in typical polyamides, both dry and containing water (see below). In addition to the expected deformation of spherulites at the crack tip,

microcracking was also shown to be major mode of deformation. Void coalescence, both continuous and discontinuous crack growth, and both transspherulitic and circumspherulitic fracture, were observed and related to the system and test conditions. The size of the process zone at the crack tip was shown to depend on ΔK^2 , in conformity with prediction.

3. The development of in-situ crystallization of an amorphous thermoplastic at the crack tip during cycling was demonstrated in studies of PET. Although this phenomenon is known to account for the resistance to FCP in natural rubber, this is the first example found for thermoplastics.

4. The role of crystallite size and perfection in FCP resistance was demonstrated using PET, whose crystallinity can be conveniently varied from zero to $\sim 40\%$. As the % crystallinity was increased from zero, FCP rates (at a given ΔK) first increased, then decreased, and then increased catastrophically for a given crystallite size. At a given % crystallinity, the FCP rate varied directly with crystallite size and perfection. A model was developed to explain these effects in terms of the effect of thermal history on the tie sequences linking crystallites (and lamellae within crystallites).

5. A beneficial effect of high molecular weight (M) on FCP resistance was shown in PET, polyacetal, and nylon 66. This finding is attributed to the great ability of high- M species to yield energy-dissipating entanglement networks in the chain sequences linking crystallites.

6. Unexpected effects of water on FCP were observed in nylon 66. As the water content was increased from zero, the FCP rate first decreased by an order of magnitude, and then increased to a value higher than that of the control. A model was developed based on a balance between beneficial localized heating and crack blunting, and deleterious generalized heating and associated modulus decrease in the bulk. The behavior was shown to be consistent with the viscoelastic spectrum as affected by water, and with measurement of temperature profiles (see below). Extension of the model to other systems has also been possible.

7. To scan temperature profiles at and beyond crack tips, special apparatus was designed involving an infrared microscope coupled with an LVDT and recorder.

8. Research on toughened, rubber-modified polymers was conducted to determine the role of a rubbery second phase. Work begun on epoxies was transferred to our NSF project, while research under this contract was focused on FCP in rubber-toughened nylon 66 as a function of rubber content and water content (see above). In general, the combination of rubber with absorbed environmental water yielded poorer FCP resistance than either component alone. As with the neat matrix, FCP behavior was correlated with the balance between localized and generalized hysteretic heating, and, fundamentally, with the viscoelastic spectrum.

9. As with the neat matrixes, the micromorphology of fracture of the rubber-modified polymers was elucidated. Whereas void coalescence was typical of dry, neat nylon 66, rumpled fracture surfaces, with secondary fissures normal to the crack, were observed. A model was

proposed to explain these fractures in terms of effects of the second phase or viscoelastic response.

Composites

1. The role of short glass fibers in the FCP resistance of semicrystalline polymeric composites was determined in nylon 66, nylon 612, polystyrene, and polypropylene. With nominally random fibers in injection-molded specimens of nylon 66, the FCP resistance increased with increasing fiber content, at least up to 30 vol. % glass. Although it had been expected that energy-dissipating micromechanisms associated with debonding and fiber pullout would have dominated the behavior, in fact the increase in modulus due to the glass was forced to be more important. Absorbed water was found to be deleterious, due either to accelerated debonding or pulling away of the matrix.

2. In contrast to the beneficial effects of fibers, the incorporation of two particulate siliceous fillers in nylon 66 and poly(methyl methacrylate) was deleterious, even though static toughness was improved. The reason was shown to lie in an enhanced sensitivity to the sharpness associated with a fatigue-induced crack.

3. The micromechanisms of fatigue failure were shown to be similar to those observed in static failure: debonding, fiber pullout, matrix crazing and cracking, and fiber breakage. However, debonding was always seen even in the early stages of crack growth, and even with well-bonded fibers that did not debond significantly in a tensile test. Thus

fatigue is clearly more severe than tensile loading with respect to interfacial integrity. At the same time, the fracture surface morphology of the fast-fracture region was the same for both fatigue and tensile specimens.

4. Increased ductility of the matrix (nylon 66 vs. polystyrene) was shown to increase the absolute FCP resistance, though the resistance relative to that of the matrix was decreased. Increased fiber length was also beneficial, though the range was small due to fiber breakage due to the injection molding process.

5. A model was developed to predict FCP resistance in terms of fiber content, interfacial adhesion, and ductility of the matrix.

6. Effects of fiber orientation and interfacial adhesion were elucidated in short-glass-fiber-reinforced polypropylene using specimens first extruded with a special die and then molded to yield essentially unidirectional fibers. In general, fibers oriented perpendicular to the crack conferred a higher threshold values of ΔK for the initiation of crack growth, higher values of FCP resistance, and higher values of the maximum ΔK attainable. However, unexpected effects of interfacial adhesion were seen. With fibers perpendicular to the crack, fiber avoidance dominated the failure, and the FCP resistance was greater, the stronger the interfacial bonding. In contrast, with fibers parallel to the crack, the crack followed the interfaces, and the FCP resistance was greater, the weaker the interfacial bonding. Indeed, microscopic examination showed that in the latter case, strong bonding inhibited the formation of the damage zone ahead of the crack, and hence restricted energy dissipation.

7. Curiously, replacement of polypropylene with rubber-toughened polypropylene resulted in lower FCP resistance than in either the control homopolymer or the fiber-reinforced plain polypropylene. It is likely that the enhanced ductility in this case causes a premature pulling away of the matrix from the fiber, with consequent loss of mechanical coupling at the interface.

Thus considerable insight has been gained with respect to the effects of second phases on fatigue crack propagation, as opposed to failure during monotonic tests. Some behavior is similar in both cases, but some is quite different. The results and models developed should be helpful in the selection of materials and design of components, and, in the case of composites, should be relevant to long-fiber systems as well.

Principal findings were published, and also communicated at various national and international meetings (see below). Presentations were also made at research review meetings held by the ONR.

PERSONNEL

The following personnel were associated with the project:

Senior Staff

Dr. R. W. Hertzberg, Professor of Materials Science and Engineering; Director, Mechanical Behavior Laboratory (Co-investigator)

Dr. J. A. Manson, Professor of Chemistry, and Materials Science and Engineering; Director, Polymer Laboratory (Co-investigator)

Dr. G. Attalla, Research engineer, Istituto Donegani; the Montedison Group, Milan, Italy (visiting scholar)

Dr. C. Murphy, Professor Chemistry, East Stroudsburg University,
(visiting scientist, summer)

Mr. G. M. Connelly, Research Engineer, Materials Research Center.

Graduate Students

P.E. Bretz, Department of Materials Science and Engineering, Ph.D.
candidate

J. C. Michel, Polymer Science and Engineering Program, Ph.D.
candidate (briefly)

M. J. Hahn, Department of Materials Science and Engineering, Ph.D.
candidate

A. Ramirez, Polymer Science and Engineering Program, Ph.D.
candidate

J. Hwang, Polymer Science and Engineering Program, Ph.D. candidate
(briefly)

P. Gaultier, visiting graduate student, University of Compiègne.

M. J. Carling, Polymer Science and Engineering Program, M.S.
candidate

HONORS

1. R. W. Hertzberg was elected Fellow of the American Society of Metals, 1984.
2. J. A. Manson and R. W. Hertzberg received jointly the J. F. and Eleanor Libsch Award for excellence in research, Lehigh University, 1983.

PUBLICATIONS

Dissertations and Theses

1. P. E. Bretz, "Fatigue Crack Propagation in Polyamides", Ph.D. Dissertation, 1980.
2. M. J. Hahn, "Fatigue Crack Propagation in Impact-Modified Nylons", Ph.D. Dissertation, 1982.

3. A. Ramirez, "Effect of Thermal History on Fatigue Crack Propagation in a Semi-Crystalline Polymer, PET", Ph.D. Dissertation, 1982.
4. M. J. Carling, "Effect of Fiber Orientation, Interfacial Adhesion and Matrix Ductility on Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Polypropylene", M.S. Report, 1985.
5. R. W. Lang, "Applicability of Linear Elastic Fracture Mechanics to Fatigue in Polymers and Short-Fiber Composites", Ph.D. Dissertation, 1984.

Books

1. "Fatigue in Engineering Plastics", R. W. Hertzberg and J. A. Manson, Academic Press, New York, 1980.
2. "Deformation and Fracture Mechanics of Engineering Materials", 2nd Edition, R. W. Hertzberg, John Wiley, New York, 1983, pp. 697.

Articles (Refereed)

1. "Interfacial Effects in Composites", J. A. Manson, Pure Appl. Chem., 57, 1667-1678 (1985).
2. "Fatigue in Rubber-Modified Epoxies and Other Polyblends", J. A. Manson, R. W. Hertzberg, G. M. Connelly and J. Hwang, in "Multi-component Polymer Materials", D. R. Paul and L. H. Sperling, Eds., Adv. Chem. Ser. 211, 291-312 (1986).
3. "Effects of Rubbery Phase and Absorbed Water on Impact-Modified Nylon 66. Part 1: Fatigue Crack Propagation Response", M. T. Hahn, R. W. Hertzberg, and J. A. Manson, J. Mater. Sci., 21, 31-38 (1986).
4. "Effects of Rubbery Phase and Absorbed Water on Impact-Modified Nylon 66. Part 2: Fractography", M. T. Hahn, R. W. Hertzberg, and J. A. Manson, J. Mater. Sci., 21, 39-45 (1986).
5. "The Influence of Temperature and Absorbed Water on Fatigue Crack Propagation in Nylon 6", M. T. Hahn, R. W. Hertzberg, J. A. Manson, and L. H. Sperling, Polymer, in press.
6. "Effects of Specimen Configuration and Frequency on Fatigue Crack Propagation in Nylon", R. W. Lang, M. T. Hahn, R. W. Hertzberg, and J. A. Manson, in "Fracture Mechanics: Fifteenth Symposium", ed. R. J. Sanford, ASTM Spec. Tech. Publ. No. 833, 1984, p. 266.
7. "Infrared Measurement of Specimen Temperature Profiles During Fatigue Crack Propagation Tests", M. T. Hahn, R. W. Hertzberg, and J. A. Manson, Rev. Scient. Inst., 54 604 (1983).

8. "Frequency and Specimen Configuration Effects on Fatigue Crack Preparation in Nylon 66", R. W. Lang, M. T. Hahn, R. W. Hertzberg, and J. A. Manson, *J. Mater. Sci. Lett.*, 3 224 (1984); longer version in *J. ASTM STP* 833, 266-283 (1984).
9. "Environment, Frequency and Temperature Effects on Fatigue in Engineering Plastics", R. W. Hertzberg and J. A. Manson, in *Proc. 27th Sagamore Army Mater. Res. Conf.*, J. B. Burke and Y. Weiss, Eds., Plenum Press, New York, 1983, p. 231.
10. "Fatigue Crack Propagation in Short-Fiber-Reinforced Composites", R. W. Lang, J. A. Manson, and R. W. Hertzberg, *ACS Adv. Chem. Ser.* 206, 261 (1984).
11. "The Effect of Molecular Weight on Fatigue Crack Propagation in Nylon 66 and Polyacetal", P. E. Bretz, R. W. Hertzberg, J. A. Manson, *J. Appl. Polym. Sci.*, 27, 1707-1717 (1982).
12. "The Application of Infrared Microscopy in the Study of Polymer Fatigue", M. T. Hahn, R. W. Hertzberg, R. W. Lang, J. A. Manson, J. C. Michel, A. Ramirez, C. M. Rimnac, and S. M. Webler, in "Deformation Yield and Fracture of Polymers", *Plastics & Rubber Inst. (London)*, 1982, p. 19.1.
13. "Effect of Test Frequency and Water Content on Localized Crack Tip Heating in Nylon 66", R. W. Hertzberg, J. A. Manson, P. E. Bretz, M. T. Hahn, and R. Lang, *Polymer*, 23, 1675-1680 (1982).
14. "Dynamic Mechanical Spectroscopy Using the Autovibron", S. M. Webler, J. A. Manson, and R. W. Lang, *Adv. Chem. Ser.* 203, 109 (1983).
15. "Characterization of an Impact-Modified Nylon 66", M. T. Hahn, R. W. Hertzberg, and J. A. Manson, *J. Mater. Sci.*, 18, 3551 (1983).
16. "Effects of Fibrous and Particulate Reinforcements on Fatigue Crack Propagation in Polyamides", R. W. Lang, J. A. Manson, and R. W. Hertzberg, *Polym. Eng. Sci.*, 22, 982 (1982).
17. "New Concepts of Interfacial Interaction in Particulate and Fibrous Composites", J. A. Manson, *Proceedings of the International Conference on Interface/Interphase in Composite Materials*, SPE (Beneluxc), Liege, 1 (1983).
18. "Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Nylon 66: Effect of Frequency", R. W. Lang, J. A. Manson, and R. W. Hertzberg, in "The Role of the Polymeric Matrix in the Processing of Structural Properties of Composite Materials", J. C. Seferis and L. Nicolais, eds., Plenum, New York, 1983, p. 377.

19. "Effect of Thermal History and Morphology on Fatigue Crack Propagation in Poly(ethylene terephthalate)", A. Ramirez, P. Gaultier, J. A. Manson, and R. W. Hertzberg, *Fatigue in Polymers, Plastics and Rubber Institute, London*, 3.1 (1983).
20. "Fatigue Crack Propagation of Amorphous Poly(ethylene terephthalate)", A. Ramirez, J. A. Manson, and R. W. Hertzberg, *Polym. Eng. Sci.*, 22, 975 (1982).
21. "Mechanisms of Fatigue Damage and Fracture in Semi-Crystalline Polymers", P. E. Bretz, R. W. Hertzberg, and J. A. Manson, *Polymer*, 22, 1272-1278 (1981).
22. "A Correlation Between Crack Growth Rate and Fracture Mode Transitions in Low Density Polyethylene", P. E. Bretz, R. W. Hertzberg, and J. A. Manson, *Polymer*, 22, 575 (1981).
23. "Comments on a Model of Fatigue Crack Growth in Polymers", R. W. Hertzberg, M. D. Skibo, J. A. Manson, and J. K. Donald, *J. Mater. Sci.*, 14, 1754 (1979).
24. "Fatigue Crack Propagation in Crystalline Polymers: Effect of Moisture in Nylon 66". 1, P. E. Bretz, R. W. Hertzberg, and J. A. Manson, *J. Mater. Sci.*, 14, 2482 (1979).
25. "Effects of Moisture on Fatigue Crack Propagation in Nylon 66". 2, P. E. Bretz, R. W. Hertzberg, J. A. Manson, and A. Ramirez, *ACS Symp. Ser.* 127, 571 (1980).
26. "Fatigue in Polymers and Composites", R. W. Hertzberg and J. A. Manson, submitted July, 1986 to Wiley-Interscience, chapter for inclusion in the *Encyclopedia of Polymer Science and Technology*, 2nd edition.

Reports and Articles (not refereed, not covered by above)

- 1*. "Fatigue Crack Propagation in Rubber-Toughened Polyacetal", G. M. Connelly, R. W. Hertzberg, and J. A. Manson, Final project report, E. I. DuPont de Nemours & Co. (1983)
2. "Effect of Matrix on Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Polypropylene", M. J. Carling, G. Attalla, J. A. Manson, and R. W. Hertzberg, *Polymer Preprints*, 26(1), 24 (1985).
3. "Effect of Fiber Orientation and Interfacial Adhesion on Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Polypropylene", M. J. Carling, J. A. Manson, G. Attalla, and R. W. Hertzberg, *Proc. 43rd Ann. Tech. Conf. of SPE, Wash., D.C.*, pp. 396-398 (1985).

*Based on an extension of this work.

PATENTS APPLIED FOR

None

PRESENTATIONS

Numerous invited presentations were made at national and international meetings and symposia of the American Chemical Society, Plastics and Rubber Institute, and the IUPAC Microsymposium on Composites. Presentations were also made at research review meetings held by the ONR at Arlington, VA, the University of Massachusetts, and Princeton University. The most recent were:

1. "Effect of Matrix in Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Polypropylene", J. A. Manson, Symposium on Composites, ACS meeting, Miami, April, 1985.
2. "Effect of Fiber Orientation and Interfacial Adhesion on Fatigue Crack Propagation in Short-Glass-Fiber-Reinforced Polypropylene", J. A. Manson, SPE ANN. Tech. Conf., April, 1985.
3. "Fatigue in Polymer Blends", J. A. Manson, Symposium on Toughening of Plastics", Plastics and Rubber Inst., London, July, 1985.
4. "Interfacial Effects in Composites", J. A. Manson, plenary lecture, IUPAC Microsymposium on Composites", Prague, July, 1985.

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