PB83-217851

Structural Basis for the Mechanical Properties of Polyethylenes

Northwestern Univ., Evanston, IL

Prepared for

Gas Research Inst., Chicago, IL

May 83

19960306 038

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
ARRADCOM, DOVER, N. J. 07801

PLASTEC

DTIC QUALITY INSPECTED 1

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
NTIS

PB83-217851

GRI-81/0132

Structural Basis For The Mechanical Properties Of Polyethylenes

Annual Report
(December, 1981 - November, 1982)

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. GRI-81/0132	2.	3. Recipient's Accession No. PB83 217851
4. Title and Subtitle STRUCTURAL BASIS FOR THE MECHANICAL PROPERTIES OF POLYETHYLENES			5. Report Date May 2, 1983
			6.
7. Author(s) S. H. Carr, B. Crist, and T. J. Marks			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Northwestern University Evanston, IL 60201			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) 5081-260-0538 (G)
12. Sponsoring Organization Name and Address Gas Research Institute 8600 W. Bryn Mawr Avenue Chicago, IL 60631			13. Type of Report & Period Covered Annual Report 12/81-11/82
			14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

The physical properties of polyethylene, the material used in gas transmission pipes, are ultimately determined by the nature of the polymeric molecules in the resin used in pipe manufacture. This relation between molecular structure and properties is based on the morphology formed in the polyethylene by a particular processing history. Model polyethylenes having very narrow molecular weight distributions and well defined levels of short chain branching and long chain branching have been used to quantify the effects of molecular structure on mechanical behavior. This first stage of the program has concentrated on true stress-true strain tensile properties and in the fracture toughness of single edge notched samples. It has been demonstrated that a critical molecular weight is required for the attainment of good ductility and fracture toughness. This critical molecular weight is increased by short chain branching and by long chain branching. The J-Integral method of analyzing fracture mechanics has been shown to be the best technique for inherently ductile polyethylenes. Measurements show a 2.5-fold increase in fracture toughness over precisely the same molecular weight range at which tensile ductility is achieved. Further work will extend our studies to lower short chain branch concentrations with model polyethylenes directly analogous to the most satisfactory resins for gas pipe applications.

17. Document Analysis a. Descriptors

Polyethylene
Molecular Weight
Short Chain Branching
Long Chain Branching
Tensile Properties
Fracture Toughness

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement: Unlimited	19. Security Class (This Report) Unclassified	21. No. of Pages 35
	20. Security Class (This Page) Unclassified	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

STRUCTURAL BASIS FOR THE MECHANICAL PROPERTIES OF POLYETHYLENES

ANNUAL REPORT

(December, 1981 - November, 1982)

Prepared by

S. H. Carr
B. Crist
T. J. Marks

Northwestern University
Evanston, IL 60201

For

GAS RESEARCH INSTITUTE

Contract No. 5081-260-0538

GRI Project Manager
Winston W. Liang
Materials Science

May, 1983

GRI DISCLAIMER

LEGAL NOTICE: This report was prepared by Northwestern University as an account of work sponsored by the Gas Research Institute (GRI). Neither GRI, members of GRI, nor any person acting on behalf of either:

a. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

b. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

RESEARCH SUMMARY

Title	Structural Basis for the Mechanical Properties of Polyethylenes
Contractor	Northwestern University GRI Contract Number: 5081-260-0538
Principal Investigators	S. H. Carr B. Crist T. J. Marks
Report Period	December 1981 - November 1982 Annual Report
Objective	To establish the molecular and morphological bases for the mechanical properties of polyethylenes.
Technical Perspective	Polyethylene piping is being used with increasing frequency for gas distribution lines. A very large variety of polyethylenes, having different characteristics, is available for the manufacture of such pipe. An understanding of the relationship between the nature of the polymer molecules, the physical morphology of the polymer, and the desired mechanical behavior is necessary for determining the mechanical reliability of polyethylene pipelines.
Results	Molecular weight has been shown to be the dominant factor controlling toughness as measured by tensile deformation or by crack propagation for the model polyethylenes. A molecular weight (MW) in excess of 70,000 is required for maximum toughness; this MW is increased by the presence of either short-chain branches or long-chain branches on the polyethylene molecules. Morphology, as evidenced by the presence or absence of spherulites, has virtually no effect on fracture behavior. The J-Integral method of fracture mechanical analysis is the best suited of available techniques for describing crack propagation in polyethylene. It was found that the fracture toughness more than doubles as the molecular weight of short-chain branched polyethylene is increased from 40,000 to 100,000.
Technical Approach	Model polyethylenes having very narrow molecular weight distributions were used for these studies; fractionated high density polyethylene and hydrogenated polybutadiene (HPB) were used. The latter are analogues for short-chain branched and long-chain branched polyethylenes. Room temperature true stress-true strain curves were generated by tensile tests on compression molded specimens. Fracture mechanics studies used single edge notched samples. These tested the Griffith, Irwin, and J-Integral methods, as well as a direct Work Integral technique in which local strains, measured by birefringence, are used to evaluate the work required for crack propagation. Morphology of these model polyethylenes was determined by microscopy, light scattering, density and calorimetry.

Project Implications

This study uses model polyethylenes with well defined chemical structures (molecular weight, short-chain branching and long-chain branching) and morphologies to identify the key parameters for controlling mechanical behavior. The first year's results indicate that molecular weight distributions and branch concentrations can be optimized to enhance the mechanical properties of polyethylenes. Additional work will be performed on the tensile and fracture properties measured as functions of crystallinity and morphology. The transition metal-catalyzed polybutadiene synthesis will be improved to obtain polyethylenes with lower concentrations of short-chain branching. To obtain a fundamental understanding of how processing techniques effect the chemical microstructure, GRI will continue to support research on model polyethylenes. This kind of research should eventually provide a basis for designing polymers having desired physical properties.

GRI Project Manager
W. W. Liang
Project Manager, Materials Science

Table of Contents

Title	Page No.
I. Overview and Introduction	1
II. Synthesis of Model Polyethylenes	3
III. Tensile Properties and Morphology of Model Polyethylenes	9
IV. Fracture Mechanical Analysis of Polyethylenes	16
V. Conclusions	26
VI. Future Work	27

I. Overview and Introduction

The goal of this research project is to establish a rational basis for the mechanical properties of polyethylene, especially those relevant to fracture behavior, in terms of the chemical microstructure, molecular weight and molecular weight distribution of the macromolecules, and morphology of semi-crystalline solids. The essential feature of this work is the use of model polyethylenes having well-defined and uniform molecular structures. With experiments on these model polymers, we are, for the first time, able to generate models for the combined effects of macromolecular architecture and morphology as they determine mechanical properties.

As direct polymerization of ethylene with or without comonomers invariably leads to mixtures of diverse molecules, we have chosen an alternative synthesis utilizing polybutadiene as an intermediate. Polybutadiene is then quantitatively saturated with hydrogen to form hydrogenated polybutadiene, HPB, which is chemically identical to polyethylene. By this scheme, we can prepare HPB analogous to polyethylene having a tailored range of molecular weights and short-chain branch concentration (models for ethylene-butene-1 copolymers) unachievable by direct synthesis. Star-shaped polymers (models for long-chain branching) can also be produced by this route.

Compression-molded films of HPB's and of other polyethylenes (fractionated high-density polyethylene, unfractionated polyethylene) are studied for tensile properties and morphology. Here our goal is to determine what morphological features are determined by the molecular parameters (e.g., short-chain branching affects crystallinity) and how these molecular/morphological effects control tensile mechanical properties.

Fracture mechanics are used to achieve an understanding of crack propagation in model polyethylenes. Considerable effort has been spent in deter-

mining which fracture analysis method adequately accounts for the behavior of polyethylene. With the variety of molecular/morphology combinations used in this study, a comprehensive model on the origin of fracture toughness is being generated.

These studies of tensile and fracture properties are done at room temperature and at a single deformation rate on compression molded samples. It is realized that temperature and rate effects and morphologies generated by alternative processing methods will influence mechanical behavior. Nevertheless, a detailed understanding of the origin of mechanical properties observed under standard conditions are necessary before consideration of additional variables.

A more complete presentation of the work done during this first year of this GRI contract is given in the following sections. Most of the results are recently obtained; interpretation of the results should be considered tentative at this time.

II. Synthesis of Model Polyethylenes

Introduction

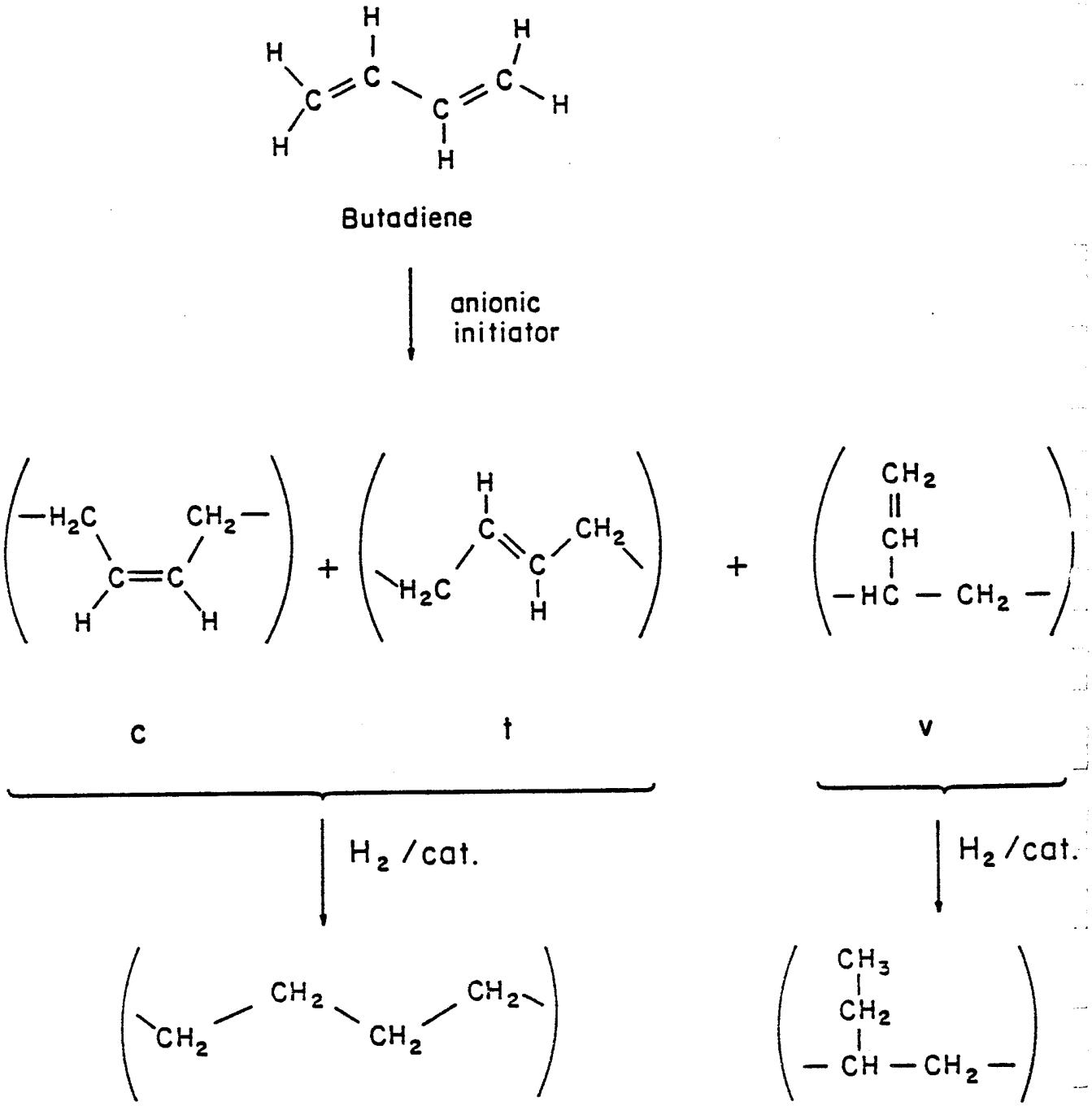
The physical properties of a polymer are largely determined by its microscopic properties, and in turn these microscopic properties are determined by the manner of preparation. Our contribution in regard to the synthetic aspect of hydrogenated polybutadienes (HPB) has been the development and refinement in the manner of preparation of polybutadiene (PB).

HPB is obtained by quantitative hydrogenation of PB which has been prepared by the reaction of butadiene monomer with an anionic initiator.[1,2] In this preparation (Figure 2-1), a number of different microstructures are obtained; cis, trans, and vinyl. Under catalytic hydrogenation conditions ($Pd/CaCO_3$), both the cis and trans microstructures result in unbranched HPB. The vinyl microstructure is hydrogenated to ethyl branches. By altering the solvent polarity in the polymerization reaction, it is possible to vary the amount of branching from ~100% to a lower limit of ~8%. With this anionic mechanism, extremely uniform molecular weights are achieved ($M_w/M_n < 1.1$).

An alternative polymerization method is that which utilizes an organo-f-element catalyst.[3-5] In contrast to the anionic polymerization, very little vinyl (<1%) microstructure is observed in polymer from this method. The predominant microstructure is cis (up to 99%)[3], which when hydrogenated results in unbranched polyethylene. The cis isomer is preferable to the trans isomer for subsequent hydrogenation, since the low melting temperature (-5°C) insures good solubility at moderate temperatures.

The organoactinide catalysts used in this method are very air-sensitive and are not commercially available. However, use of high vacuum line and glove box techniques should make synthesis of such catalysts possible.

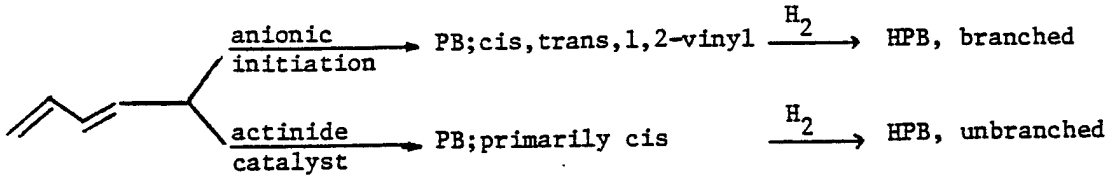
Thus, these two methods will allow comparison of the physical properties



c = cis 1-4
t = trans 1-4
v = vinyl 1-2

Fig. 2-1. Preparation of HPB via anionic polymerization.

of branched versus relatively unbranched polymer. Our



contribution to this project in the preparation of PB by these two methods, employing state-of-the-art synthetic techniques which ensure rigorous exclusion of impurities and, therefore, polymer products of maximum purity.

Results and Discussion

In the anionic method, PB is prepared from butadiene in cyclohexane solvent and an initiator (sec-butyllithium). Since both the initiator and the living polymer are highly air-sensitive, traces of oxygen or moisture affect the reproducibility of polymer synthesis, especially in preparations requiring longer reaction times. The initiator, by nature of its air-sensitivity, continuously degrades in activity. Thus, another factor affecting the reproducibility of these preparations is the uncertainty in the activity (concentration) of the initiator. These three factors, oxygen, moisture, and uncertainty of initiator activity, pose problems in the reproducible preparation of PB. Our improved method of PB preparation overcame these difficulties.

Oxygen and moisture were removed from the reaction vessel by heating (flaming) under high ($1x10^{-5}$ torr) vacuum. Trace organic contaminants (unsaturated components) were removed from the cyclohexane by stirring over concentrated H_2SO_4 for 1 day. Oxidizable contaminants were removed by stirring (1 day) over a saturated aqueous solution of $KMnO_4$. Initial drying of the solvent was accomplished by allowing the solvent to stand 8 hrs. over anhydrous $CaSO_4$. Oxygen and the last traces of water were removed from the solvent by distillation from Na/K alloy under an atmosphere of purest argon. Butadiene monomer was purified by passage through a column of supported MnO (to remove O_2) and a

column of Davison 4-Å molecular sieves (to remove H_2O). Less volatile impurities were removed by a $-40^{\circ}C$ trap (acetonitrile slush). Both solvent and monomer were vacuum transferred into the reaction vessel to eliminate exposure to air and to separate these components from less volatile ones. The initiator, the concentration of which was determined to ±0.03 M by titration with diphenylacetic acid (in dry, oxygen free THF) under argon to a yellow endpoint, was added to the reaction flask via syringe under an argon flush. As shown in Figure 2-2, the reaction flask consisted of a vessel with a grease-free "solv-seal" joint capable of holding a high vacuum. Thus, by using high vacuum techniques the problem of decomposition of the initiator and living polymer is minimized. The uncertainty in the initiator concentration is minimized by the titration procedure. As an example of this, a polymerization was run with a predicted molecular weight (based on initiator and monomer concentration) of 160,000. The molecular weight measured by gel permeation chromatography was MW = 155,900. We are currently scaling up reactor vessels so as to produce ~20 g of PB per run.

Having worked out the preparation of the branched (anionic preparation) PB, we directed our efforts toward preparing the unbranched material (the organoactinide catalyst). A number of uranium compounds including $U(n\text{-}C_3H_5)_4$, $U(n\text{-}C_3H_5)_3X$, and various alkoxides of uranium show high catalytic activity in the stereoregular polymerization of butadiene.[3-5] Our previous work with compounds of the type $(C_5(CH_3)_5)_2UR_2$ (R = alkyl group) show them to be highly reactive toward C-X, O-H, H-H, C≡O, and other functionalities.[6,7] Since the reaction of butadiene with compounds of this type (which are potent catalysts for a number of other olefin reactions) has never been studied and since we wanted to know if the catalytic activity extended to this series of compounds, we decided to examine this reaction. We found, however, with a representative compound, $(C_5(CH_3)_5)_2U(CH_3)_2$, the polymerization of butadiene was exceedingly slow. Thus, our most recent efforts are directed toward work with the known catalysts.

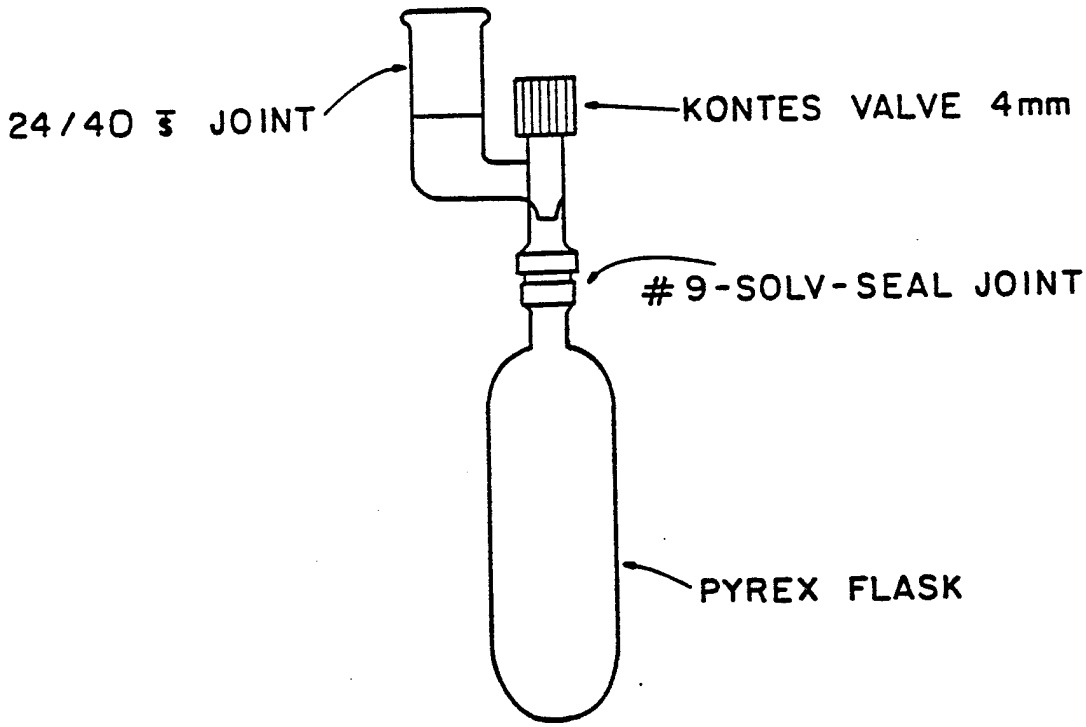


Figure 2-2. Reaction vessel for polymerization.

The preparation of organoactinide catalysts requires strict exclusion of atmospheric oxygen and moisture due to their extreme air-sensitivity. Thermal instability poses further synthetic constraints. For instance, solutions of $U(n\text{-}C_3H_5)_4$ decompose above 20°C. In order to successfully prepare

these compounds on a routine basis, a dedicated high vacuum line is needed. The line has been designed and is in the final stages of construction. Once complete, it will achieve a vacuum of better than $1x10^{-5}$ mm. It is designed with oxygen and moisture scavenging columns to deliver pure monomer feed gases, as well as inert gases. It has a solvent manifold section that allows for the introduction of a variety of solvents for preparations. Overall, it will be a versatile line for both catalyst preparation and polymerization reactions.

In conclusion, we have developed and refined a preparation of PB that insures better reproducibility in the preparation of the branched HPB for our branched versus unbranched polymers. During the period covered in this report, 5 ionic polymerizations were performed to yield polybutadienes with molecular weights varying from 8,000 to 100,000. These polymers were prepared toward the end of the report period, and are not the precursors for the HPB tested in Section III and IV. We need yet to prepare the unbranched material via a uranium catalyst. The work on the high vacuum line to be used to make the catalyst for this material is near completion.

References

1. E. Rochefort, G. G. Smith, H. Rachapudy, V. R. Raju, and W. W. Graessley, J. Polym. Sci.-Polym. Phys. Ed., 17, 1197 (1979).

2. H. Rachapudy, G. G. Smith, V. R. Raju, and W. W. Graessley, J. Polym. Sci.-Polym. Phys. Ed., 17, 1211 (1979).

3. G. Lugli, A. Mazzei, and S. Poggio, Makromol. Chem., 175, 2021 (1974).

4. M. Bruzzone, A. Mazzei, and G. Giuliani, Rubber Chem. Technol., 47, 1175 (1974).

5. F. Wang, A. Bolognesi, A. Immirzi, and L. Porri, Makromol. Chem., 182, 3617 (1981).

6. P. J. Fagan, J. M. Manriquez, E. A. Maata, A. M. Seyam, and T. J. Marks, J. Am. Chem. Soc., 103, 6650 (1981).

7. P. J. Fagan, E. A. Maatta, and T. J. Marks, ACS Symp. Ser., 152, 53 (1981).

III. Tensile Properties and Morphology of Model Polyethylenes

Introduction

It is essential to recognize that semicrystalline polymers, such as polyethylene, exhibit great ductility before ultimate failure. Even macroscopically brittle failures involve large amounts of local plastic deformation. A corollary is that it is not the initial structure which fractures, but the morphology created by the plastic deformation before fracture. This phase of the research is designed to assess the effects of molecular weight and chemical microstructure on the morphology and tensile properties of polyethylene. The rationale behind this study is that the local deformation near a crack tip, that deformation which controls the subsequent advance of the crack, can be understood through examination of tensile deformation.

Materials

The model polyethylenes used in this work are based on monodisperse preparations of three-arm star hydrogenated polybutadienes (3S-HPB) or fractionated high density polyethylene from the National Bureau of Standards (NBS). These were tested as monodisperse polymers or as bimodal blends prepared mixing high and low molecular weight polymers in solution. The molecular weight ranges of the tested polymers are presented in Table 3-1.

Table 3-1
Molecular Weights of Tensile Samples

Polymer	Mol. Wt. Range
3S-HPB, monodisperse	22,700 - 161,000
3S-HPB, blends of 22,700 - 161,000	50,000 - 132,000
NBS, monodisperse	32,100 - 119,000
NBS, blends of 13,000 - 119,000	32,000 - 93,000

In this section, we also report results obtained in these laboratories on

monodisperse and blended polymers of linear hydrogenated polybutadiene, L-HPB, having molecular weights between 13,500 and 200,000.[1] The long-chain branched and linear HPB's all have an ethyl branch concentration of 18 branches/1000 backbone C atoms, resulting in a crystallinity of ~42%. The NBS polyethylenes have crystallinity in the range of 50%-70%.

The HPB's used in this work, both L-HPB and 3S-HPB, were prepared from polybutadienes which had been synthesized prior to the start of this GRI contract.

Experimental

Films of thickness t = 0.10-0.15 mm were compression molded at 150°C and quenched in ice water. These were cut into dog-bone shape microtensile specimens with a gauge section having width w = 2.0 mm and length l = 19.5 mm. Fiducial marks were inked across the gauge section at 2 mm intervals. Tensile tests were done on a table model Instron with a crosshead speed of 0.2 in/min corresponding to a nominal strain rate of 0.26/min. A key feature of these experiments was 35 mm photographs taken of the deforming sample so as to monitor the dimensions during inhomogeneous plastic deformation. Using these data, true stress-true strain curves could be generated from the Instron curves. This testing was done at room temperature (24°C±2°C), but the lighting system for photography raised the sample temperature by about 2°C.

Results and Discussion

As the elastic modulus of a polymer involves the response to small displacements, one might anticipate that the detailed nature of the chains in a semicrystalline polymer are relatively unimportant in the small strain limit. This idea is supported by the data in Figure 3-1, which shows that the tensile modulus E correlates very well with density for linear NBS polyethylene, short-chain branched L-HPB and long-and short-chain branched 3S-HPB polymers

having a variety of molecular weights and molecular weight distributions. The straight line is from the earlier work of Sperati, et al.[2] This correlation is consistent with a logarithmic mixing law for the properties of a two-phase composite, as proposed by Gray and McCrum:[3]

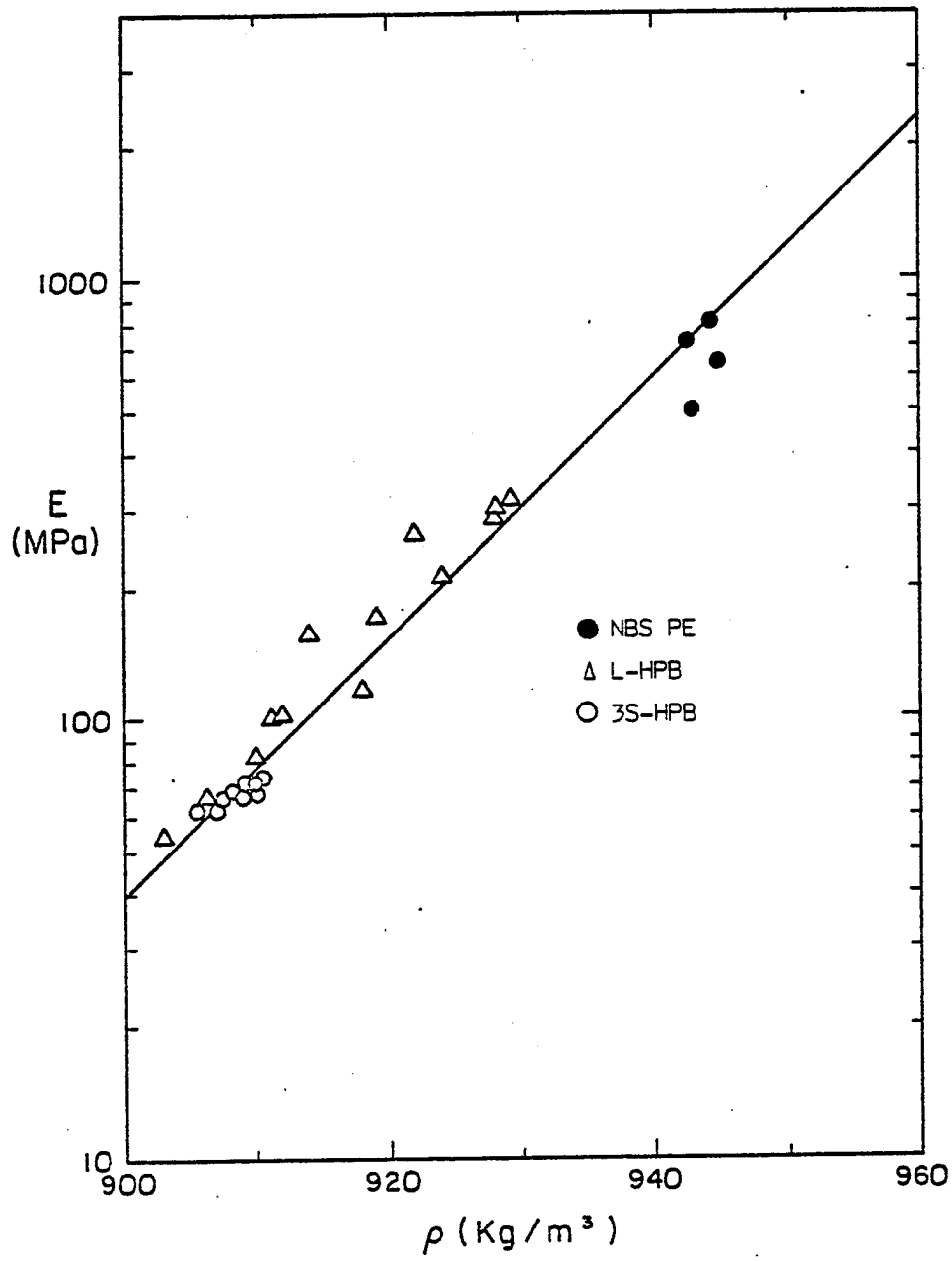


Fig. 3-1. Elastic modulus as a function of density for model polyethylenes.

$$\text{Log}E = \alpha \log E_c + (1-\alpha)\log E_a \qquad (3\text{-}1)$$

Here α is the volume fraction crystallinity (proportional to the density) and E_c and E_a are the elastic moduli of the crystalline and amorphous regions, respectively. Extrapolating the data to $\alpha = 0$ and $\alpha = 1$, one obtains $E_a = 120$ MPa and $E_c = 4200$ MPa. The latter figure compares reasonably well with the Reuss (constant stress) average theoretical value $E_c = 5300$ MPa $\pm$ 500 MPa calculated for isotropic, crystalline polyethylene by Odajima and Maeda.[4] These findings demonstrate that the elastic nature of the two phases in polyethylene, as reflected in E_a and E_c, is independent of molecular weight and short or long chain branching.

The mechanical behavior at larger deformations, on the other hand, is quite sensitive to the types of molecules in the solid. An increase in ductility is observed on increasing molecular weight, the critical value of MW for this transition rising from ~50,000 (unbranched NBS PE) through ~70,000 (short chain branched L-HPB) to 100,000 (long and short chain branched 3S-HPB). These effects are seen in Figure 3-2, in which the engineering failure strain e_f is plotted as a function of molecular weight for the three types of model polyethylenes. The dashed line (a) in that figure summarizes the results of Fulmer and Horowitz;[5] our more limited data agrees with theirs quite well. A tentative interpretation of these effects is based on the formation of enough intercrystalline tie molecules to support high extensions. A major effect of short chain branching is to decrease the crystallinity; if the intercrystalline amorphous thickness is increased, by the presence of ethyl branches, larger molecules are required to bridge the larger gap. Long chain branching <u>decreases</u> the physical size of a macromolecule of the same molecular weight; this is believed to dominate the shift to higher MW required for 3S-HPB to achieve the same elongation. More detailed studies are underway to support these hypotheses.

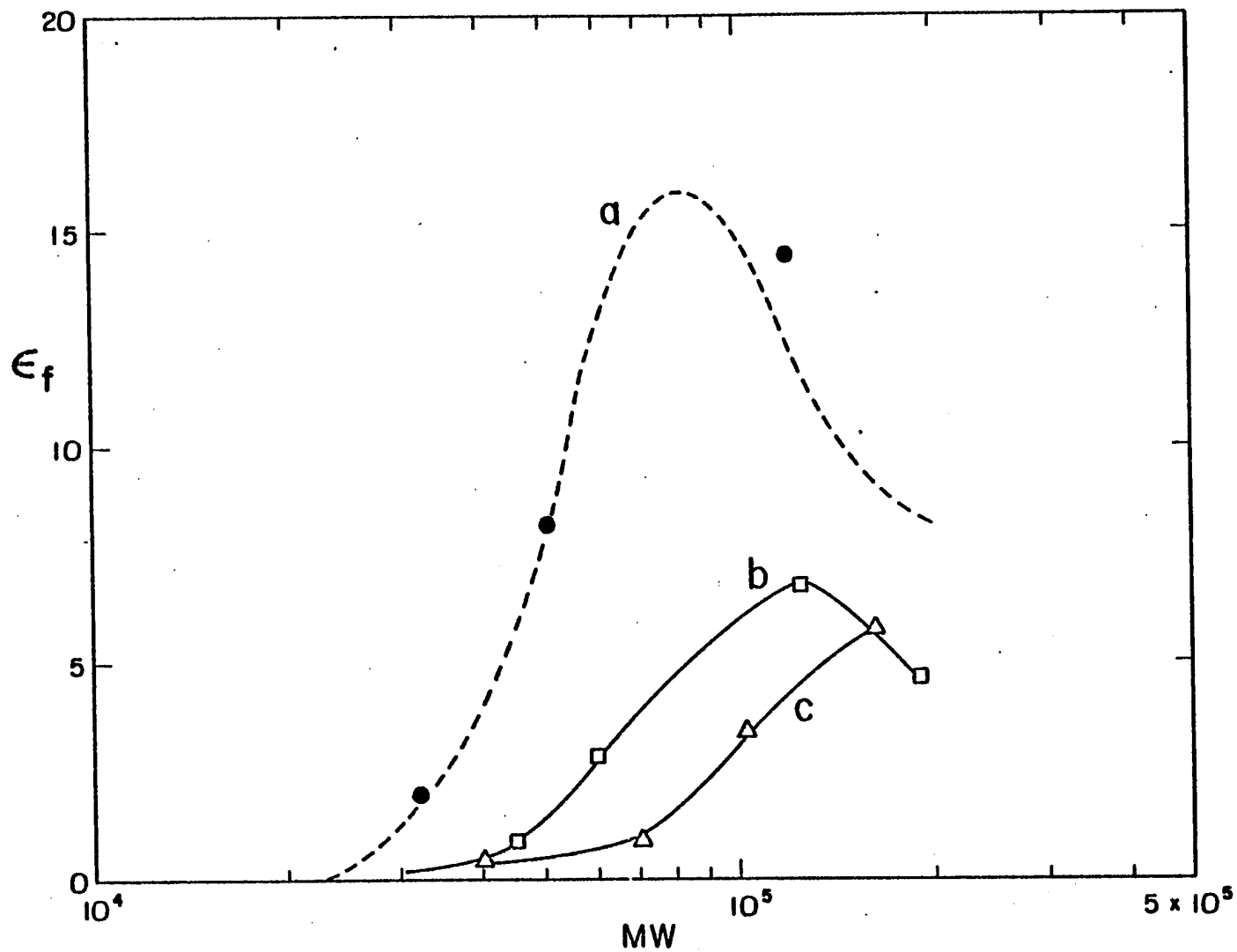


Fig. 3-2. Tensile failure strain vs. molecular weight for (a) NBS PE; (b) L-HPB; (c) 3S-HPB. The dashed line is from ref. 5.

The HPB model polyethylenes, especially the three-arm star polymers, have crystallinities which are virtually independent of molecular weight. This leads to the remarkable data in Figure 3-3, in which true stress is plotted against true strain for tensile deformation of 3S-HPB having different molecular weights. The singular feature of this graph is the fact that molecular weight affects only the maximum strain which a particular polymer can sustain. There is a single stress-strain curve and mechanical response for this set of polymers; the fracture point is the only property influenced by molecular weight. Preliminary morphology studies on this series of 3S-HPB's show that ~5 μm diameter spherulites form for MW $<$ 100,000, while no spherulites are formed at higher molecular weights. Thus, it can be concluded that morphology on the spherulitic level does not control the intrinsic deformation mechanisms of these polyethylenes.

References

1. P. Howard and B. Crist, unpublished results.

2. C. A. Sperati, W. W. Frank, and H. W. Starkweather, Jr., J. Am. Chem. Soc., 75, 6127 (1953).

3. R. W. Gray and N. G. McCrum, J. Polym. Sci. A-2, 7, 1229 (1969).

4. A. Odajima and T. Maeda, J. Polym. Sci., C15, 55 (1966).

5. G. E. Fulmer and R. H. Horowitz, Proc. VII Intrl. Cong. Rheology, Gotherburg, 624-625 (1976).

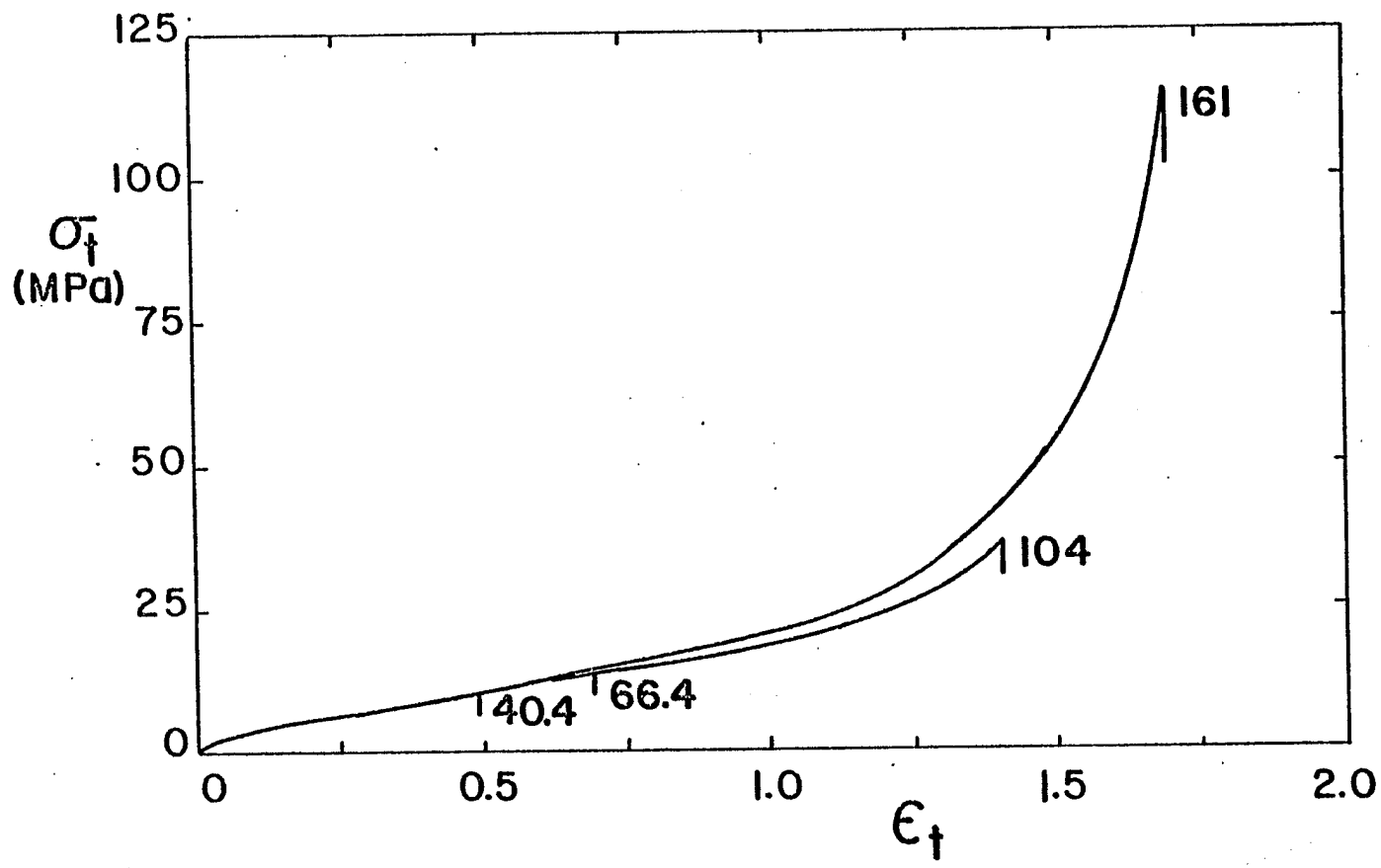


Fig. 3-3. True stress - true strain curves for 3S-HPB monodispers polymers.

IV. Fracture Mechanical Analysis of Polyethylenes

Introduction

The purpose of fracture mechanical analyses of materials is to understand the relationships between intrinsic material properties and the geometry of the specimen into which that material has been made. The intrinsic material properties include such parameters as elastic modulus, E, yield point (yield stress, yield strain), the response of the material to complex states of stress, and the stability (or lack thereof) of cracks in these materials. It is with regard to this latter set of parameters that fracture mechanics is most directly focused. The ultimate ambition in fracture mechanical analysis is to find a way to express these parameters in terms of a single number for each material. The ways to combine the parameters into such a single number has involved theoretical work by many people over a considerable period of time, and the fruits of their work are the various fracture laws, one of the earliest and most famous of which is the Griffith crack criterion. Recent efforts, such as the J-integral theory, are more successful in providing a single number for each material.

The essence of these theories is to equate the work put into the specimen with the driving force for propagating a crack, given that an embryonic crack exists in the specimen. There are numerous ways to formulate this equation, and they are not the subject of this paper at the present time. The following sections in this chapter, however, will show how the J-integral analysis compares with the Irwin fracture toughness analysis. The Irwin analysis is more simple to perform and is reasonably straightforward in its concept. However, as will be seen in the following sections, it is unable to produce a single parameter that characterizes the way polyethylenes (at least these model polyethylenes) behave in terms of the stability of cracks such specimens may contain. An alternative method, what we call the "Work Integral" analysis,

has also been employed. It is a "brute force" method, in that it uses optical microscopy to analyze directly the strain field produced around the crack tip; these strains are used to evaluate the work increment needed to build the plastic zone which forms at the tips of cracks. This method can plausibly be regarded as one which could come up with a single fracture mechanical parameter and, in addition, it is able to visualize the strain field such that the exact mechanisms of crack advancement may be discovered by direct observation. This includes information on the amount of crack tip blunting, the relative amounts of normal stress yielding versus shear stress yielding that might occur in the plastic zone, and the possible role of void formation in advance of the crack tip.

Therefore, it is the thrust of this work to accomplish two tasks: the first is to determine which fracture mechanical laws are successful in characterizing fracture toughness in polyethylenes. The second is to develop a detailed understanding of fracture in polyethylene materials on the basis of molecular parameters of the polymer itself. With regard to the former objective, there is reason to believe that the unusually high levels of ductility so common with semicrystalline polymers might render inapplicable one or more of the existing fracture mechanical theories. The reason for this is simple: the fracture mechanical laws are developed for nonpolymeric materials which, almost without exception, lack the ductility levels we are talking about here. As will be seen, however, the J-Integral analysis is successful for the materials we have been studying. With regard to the second objective, it appears that there is a very strong molecular weight dependence to the fracture toughness parameters in question, and thus it is anticipated, at this point, that the architecture of the molecules in a polymer sample will indeed have a strong influence over the fracture toughness of these materials.

EXPERIMENTAL

Specimens for fracture mechanic studies were prepared from L-HPB having molecular weights from 43,600 to 102,000. Tensile samples were cut from compression molded films in a manner similar to that described in Section III. Notches of different lengths were cut from the edge using a point tip scalpel blade. Notch size was measured with a calibrated optical microscope. Notched and unnotched samples were deformed at room temperature with the table model Instron at a nominal strain rate of 0.22/min. The mechanical work required to achieve different macroscopic strain levels was evaluated by integration of the force-elongation curves.

Specimens for strain-optical studies required more specialized techniques outlined below.

1. Calibration samples

HPB's were compression molded and cut into tensile samples for obtaining strain optical coefficients. These samples had a gauge length of 20.5-22.8 mm, a width of 2.0-2.2 mm, and a thickness of 0.10-0.18 mm. They were mounted on a tensile device which fit on the stage of a Leitz Ortholux optical microscope equipped with crossed polarizers. The retardation at different values of nominal strain was measured using a Leitz Berek Compensator. The width of the samples at these strain values was measured using a Bausch & Lomb optical micrometer.

The thickness of the strained samples was calculated assuming a Poisson's ratio of 0.5, i.e., constant volume deformation, and the birefringence was obtained by dividing the retardation by the thickness. "Pre-yield" and "post-yield" strain optical coefficients were then obtained for each sample by plotting birefringence versus nominal strain.

2. Specimens for Work Integral Analysis

A gold grid was evaporated on some prenotched samples using a vacuum evaporator. A 300 mesh copper grid was placed on the samples around the crack tip, and then a thin (ca. 150Å) layer of gold was deposited over the specimen. This produced an orthogonal array of evaporated gold squares in the zone around the crack tip.

Samples were then mounted on the tensile stage for the optical microscope and the retardation was measured at different locations around the crack tip, at an overall nominal specimen strain of 0.05. Pictures of these samples were taken before and after they had been strained using an Olympus C-35-A Camera. The change in the area of each differential volume was measured from the pictures, and assuming a Poisson's ratio of 0.5, the local thickness was calculated. This allowed for the evaluation of the birefringence at each differential volume around the crack tip. These birefringence values were then translated into local strain values using the strain optical coefficients.

RESULTS AND DISCUSSION

1. J_{Ic} Integral Analysis[1]

The work, U, per unit thickness, T, was evaluated for each notched sample at different specimen elongation values, ΔL. The ratio, U/T, was plotted against initial crack length, a_o at various constant ΔL values. A typical graph is shown in Figure 4-1. The Davidou-Fletcher-Powel[2] minimization method was used to obtain a least squares fit of a parabola to the experimental Data. Differentiation of the obtained equations yielded the J values as a function of initial crack size for the different ΔL values:

$$J = \left.\frac{d(U/T)}{da_o}\right|_{\Delta L}$$

A plot of J versus ΔL was then constructed for different crack sizes. As

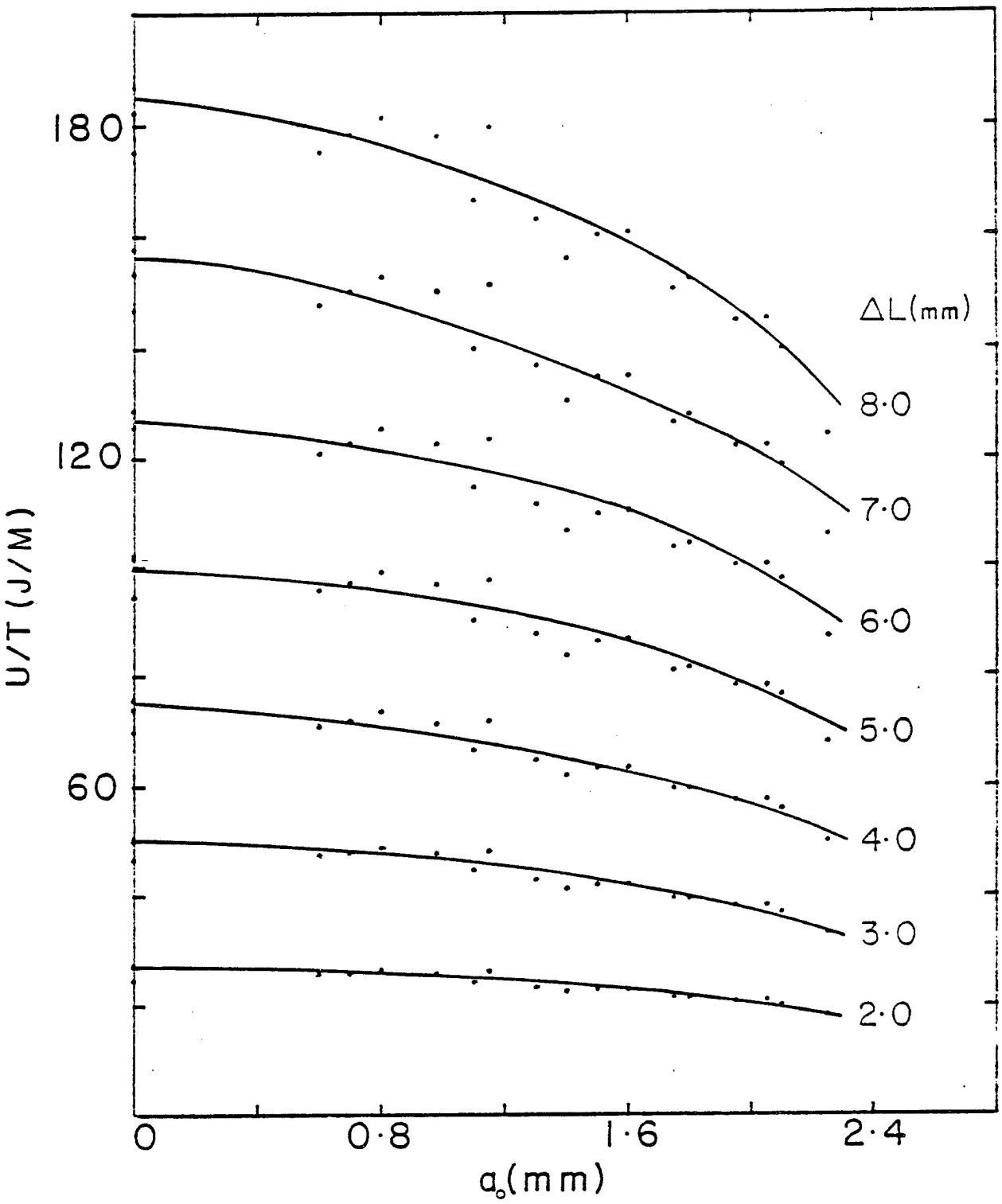


Fig. 4-1. U/T versus a for $M_n = 92,000$

shown in Figure 4-2, the curves were found to conform to the shape predicted by the theory,[3] i.e., at low ΔL values J was proportional to $(\Delta L)^2$, while at higher ΔL values a linear dependence of J on ΔL was obtained. A linear regression analysis was performed on this linear portion of the curves, and a J_{Ic} value for each sample was finally obtained by substituting the displacement value at which crack propagation initiated into the obtained linear relationships. The ΔL value at which crack propagation commenced was assumed to be the point at which load on the specimen reached its maximum, as suggested by Landes and Begley.[3]

Although the J versus ΔL curves varied with initial crack size, fairly constant J_{Ic} values were obtained for each set of samples. Such results, for four different molecular weights, are summarized in the Table below.

Table 4-1

M.wt.	J_{Ic} (KJ/m^2)	Standard Deviation
43,600	18.6	2.6
63,000	16.4	2.1
92,000	46.5	6.2
102,000	44.6	5.3

One can infer from these data that toughness in monodisperse polymer materials develops abruptly as molecular weight goes up. It is most significant to note, furthermore, that toughness sets in at molecular weights immediately above those capable of exhibiting full levels of ductility.

G_{Ic} Analysis

The two factors of importance in the Irwin fracture toughness[4] analysis are: the critical stress intensity factor, K_{Ic}, and the fracture toughness parameter, G_{Ic}. These are given by the following equations.

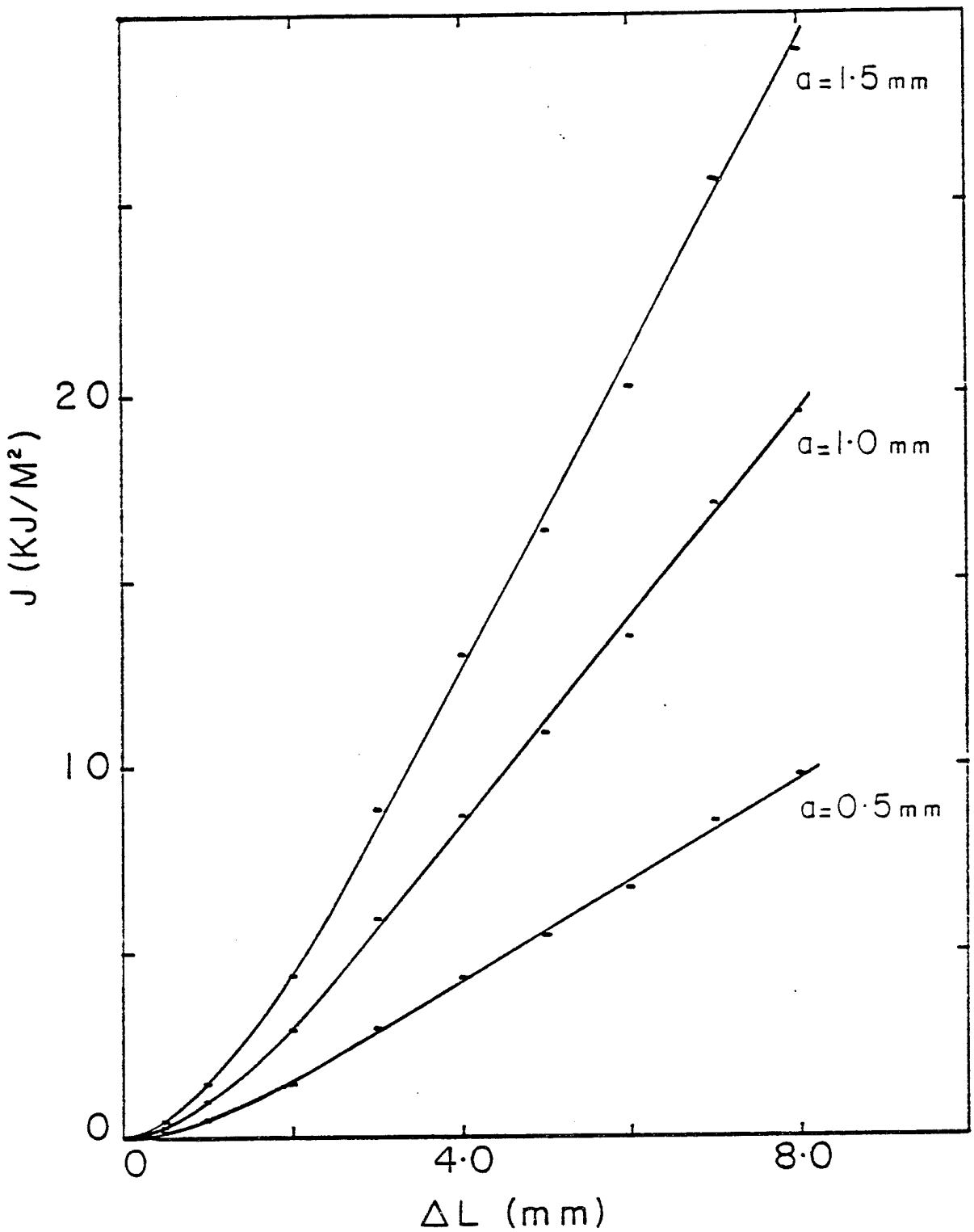


Fig. 4-2. J versus ΔL for $M_n = 92{,}000$

$$K_{Ic} = \sigma_c (\pi a_o)^{\frac{1}{2}} f(a_o/b) \tag{4-1}$$

$$G_{Ic} = \frac{K_{Ic}^2}{E'} \tag{4-2}$$

where σ_c is the stress value at which crack propagation initiates, a_o is the initial crack size, b is half the width of the sample, f(a/b) is a correction factor as given by Paris and Sih,[5] and

$$E' = \begin{cases} E \text{ for plane stress} \\ \frac{E}{1-\nu} \text{ for plane strain} \end{cases}$$

where E is the elastic modulus, and ν is Poisson's ratio. The values of σ_c and E were obtained from the load-extension experiments, and K_{Ic} and G_{Ic} were evaluated using equations (4-1) and (4-2), respectively.

The plot of G_{Ic} versus a_o in Figure 4-3 shows the strong dependence of this toughness parameter on the initial crack size. One must, therefore, regard the J integral analysis as more advantageous than the G analysis, due to the independence of J_{Ic} on geometry and crack size.

Work Integral Analysis[6]

Computation of the work needed to build the plastic zone ahead of a growing crack involves point-by-point measurement of birefringence throughout the plastic zone and the conversion of those birefringence values into quantities of work needed to reach such levels of birefringence.

The local strain value obtained at each element of volume around the crack tip, as explained in the experimental section, was translated into a work per unit volume, W_i, using strain-optical coefficients obtained from load-extension experiments on unnotched HPB specimens of each molecular weight listed in Table 4-1. The plastic zone was defined by the area where there was a birefringence gradient relative to the crack tip.

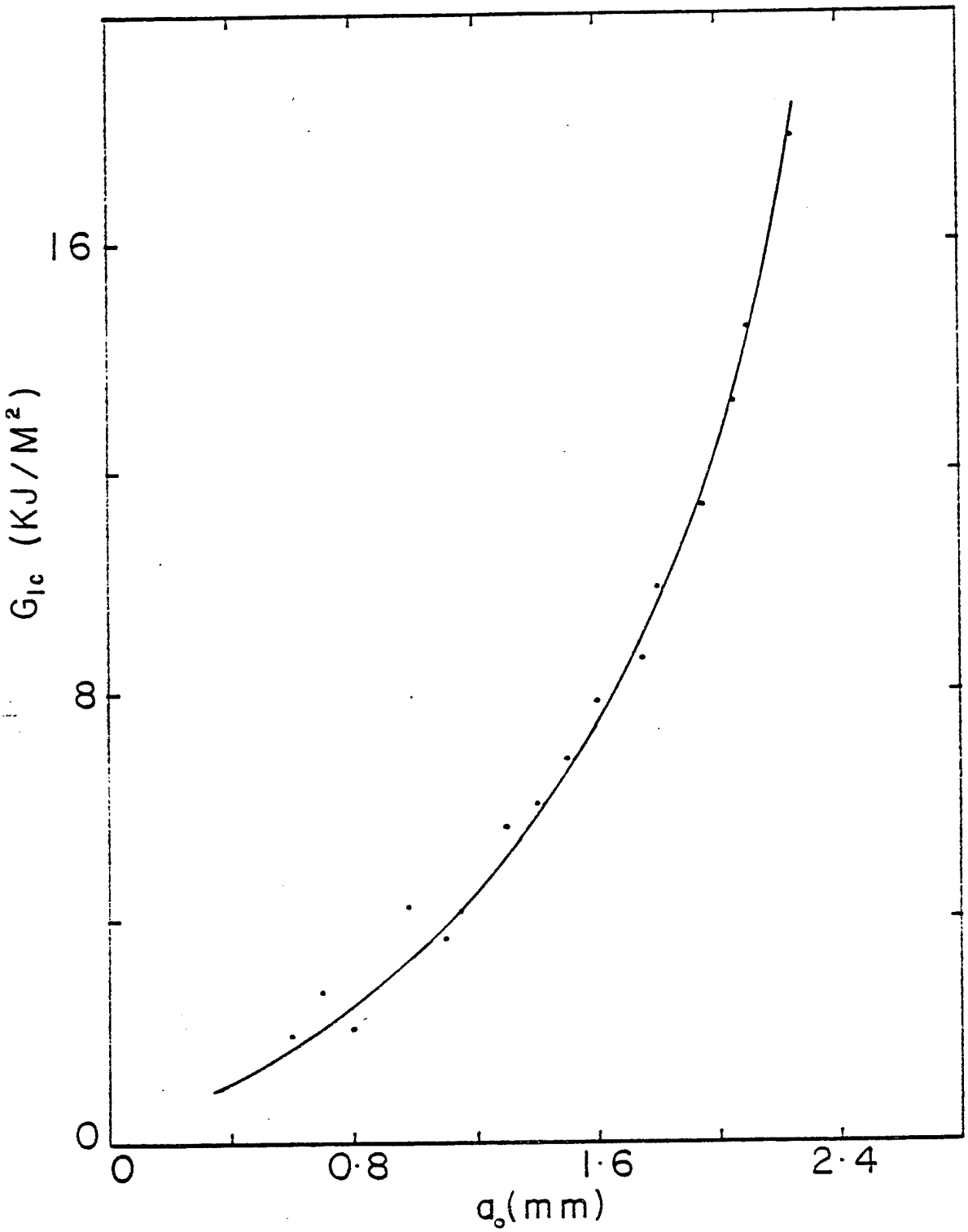


Fig. 4-3. G_{Ic} versus a_o for $M_n = 92,000$

Each of these energies per unit volume were multiplied by its respective differential volume, v_i, and the values thusly derived were combined to yield the total amount of work, W_T, stored and/or dissipated in the plastic zone around the crack tip:

$$W_T = \sum_i W_i v_i$$

where i refers to the individual differential volumes. This integrated energy value is found to be about two and a half times larger than the work which would have been dissipated and/or stored in the same volume, had the crack not been present. In other words, the work was intensified by a factor of about 2.5 in the plastic zone, due to the presence of the crack.

REFERENCES

1. J. R. Rice, J. Appl. Mech. Trans. 35, 379 (1968).

2. David M. Himmelblau, Applied Nonlinear Programming, McGraw Hill, New York, 1972, p. 111.

3. J. D. Landes and J. A. Begley, in Proc. 1971 Natl. Symp. Fracture Mechanics, ASTM, STP 514, Am. Soc. Test. Matls., Phila., PA, 1972, p. 24.

4. H. Tada, P. C. Paris, and G. R. Irwin, The Stress Analysis of Cracks Handbook, Del Research Corp., St. Louis, MO, 1977, p. 2.10 ff.

5. P. C. Paris and G. C. Sih, in Progress in Flaw Growth and Fracture Toughness Testing, ASTM, STP 381, Am. Soc. Test. Matls., Phila, PA, 1965, p. 30.

6. W. R. Even and S. H. Carr, Polymer 19, 583 (1978).

V. Conclusions

The following points have been established during this year's research on the mechanical properties of polyethylenes:

- The anionic polymerization of butadiene used in our synthesis of model polyethylenes is improved by careful control of inpurities in reactants and solvents.
- Molecular weight has a pronounced effect on the tensile properties of polyethylene. The molecular weight required to achieve good ductility and toughness increases with both short chain branching and long chain branching.
- The nature of the spherulitic morphology has little or no effect on tensile properties of polyethylene. Crystallinity seems to dominate the elastic modulus.
- The J-Integral fracture mechanics analysis is most suitable for studies of polyethylene. Simpler methods such as the Griffith or Irwin techniques are inadequate.
- Molecular weight has a strong effect on fracture toughness. High fracture toughness is developed in notched specimens at about the same molecular weight required for large ductility in tensile tests.

VI. Future Work

The second year of this research project will focus on the following tasks:

- Develop the transition metal-catalyzed polybutadiene synthesis so as to obtain model polyethylenes with lower concentrations of short chain branching. This is essential for the study of more crystalline materials which are analogues for the high and medium density polyethylenes used in pipe manufacture.
- Extend tensile, fracture mechanics and morphology studies to the higher density polyethylenes.
- Evaluate the effects of broader distributions of molecular weight on mechanical properties. Preliminary tests with bimodal blends and a few whole polymers indicate that results can be compared on the basis of weight average molecular weights.
- Investigate the morphological changes occurring during deformation. These experiments are necessary for understanding the origin of fracture properties, especially toughness. Microbeam techniques will be employed with X-ray and light scattering studies of deformation. Optical and/or electron microscopy will be used to determine the nature of crack propagation by the study of fracture paths and fracture surfaces.
- Complete the complementary tensile (Section III) and fracture studies (Section IV) on available materials. This will enable us to define more quantitatively the relation between stress-strain properties and fracture toughness. Furthermore, this information will guide us in the types of model polyethylenes being synthesized (Section II) to optimize properties.