

INTERNATIONAL SYMPOSIUM
on
**Approaches to
Property Limits in
Polymers**

ABSTRACTS

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CALCULATIONS ON RIGID AROMATIC HETEROCYCLIC POLYMERS. J. E. Mark. Department
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Some aromatic heterocyclic polymers are sufficiently rigid to form anisotropic (liquid-crystalline) phases, and precipitated films and fibers of these materials exhibit high tensile strengths, good thermal oxidative stabilities, and resistance to most common solvents. Hence these materials are of particular interest in applications where high-performance characteristics are required. Conformational energy calculations were carried out on such polymers in order to determine whether or not the molecules are planar and if not, the extent of their nonplanarity. Such information is highly relevant to the nature of the chain packing in the crystalline and liquid-crystalline states. Intermolecular interactions were also investigated, both with regard to their effect on the extent to which the chains approach the desired coplanar conformation, and with regard to the origin of the high mechanical strengths of these materials. The same types of calculations were used to characterize the flexibility of molecular swivels introduced into these chains in order to facilitate their processing. Finally, electronic band structure calculations were carried out for several chains.

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CONFORMATIONAL ORDERING IN SEMIFLEXIBLE POLYMERS. Do Y. Yoon, IBM Almaden Research Center, San Jose, California 95120.

Difficulty of packing long chain molecules to high density results in the occurrence of an ordered state in concentrated solutions and in the bulk of polymers with insufficient flexibility, in contrast to the well-established observation of random-coils of flexible polymers at all concentrations. Anisotropic interactions favoring parallel alignments of neighboring segments, usually present in semiflexible polymers, further promote the ordered state over the disordered state of random chains. This ordering in semiflexible polymers is distinguished, most importantly, from that of rodlike molecules in that it entails a rather drastic change of chain conformations from the random-coils in the disordered state to highly extended pseudo-rodlike conformations in the ordered state. Theoretical calculations on lattice chains and experimental results on aromatic polyimides and thermotropic nematic polymers will be presented to describe this conformational ordering in semiflexible polymers and its consequences on polymer properties.

IDEAL STRENGTH OF COVALENTLY BOUND SOLIDS
WITH SPECIAL REFERENCE TO POLYMERS

A Kelly and N H Macmillan
University of Surrey and the Pennsylvania State University

Calculations of the theoretical tensile strength and of the Young's modulus of linear polymers will be reviewed. The values will be compared with the highest reliable experimental values known to the authors.

The possibility of shear limiting the strengths of carbon and similar fibres will be discussed as well as the effects of surface defects on attainable strengths.

The work of fracture of very strong polymer fibres is of some interest, and can be modelled as a type of aligned fibre composite failing by pull out of fibres. This idea is explored in order to find values of the cohesive forces between long chain molecules.

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GROWTH MECHANISM, PROPERTIES AND PRACTICAL LIMITS OF WHISKER MATERIALS,
John V. Milewski, P.O. Box 8029, Santa Fe, New Mexico 87504-8029.

This paper starts by defining a whisker and then it gives a brief history of how and where whiskers were discovered and the name given. This is followed by a review of the general properties of various whisker materials. Next, the various growth mechanisms are discussed, (e.g. tip vs. base growth with details given on the spiral dislocation and V.L.S. processes). The details of how an individual whisker is tensile-tested is then presented. Finally, the theories or practical limits and ultimate properties are reviewed.

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THE DEFORMATION OF SEMI-CRYSTALLINE POLYMERS. Leo Mandelkern and Rakesh Popli, Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306.

A set of independent structural variables, characteristic of semi-crystalline polymers, which depend on molecular weight, molecular constitution and crystallization conditions and which control many different properties, has been described previously. The strategy developed of isolating these variables has now been directed to the study of the mechanical behavior of crystalline polymers including force-length relations and ultimate properties. A series of polyethylenes, representing a wide range in molecular structures and in values of the key independent variables, have been studied. The dependence of the key mechanical properties, such as initial modulus, yield stress, ultimate draw ratio and tensile stress at break, on these variables has been established and the beginning of a molecular understanding is emerging.

A.H. Windle

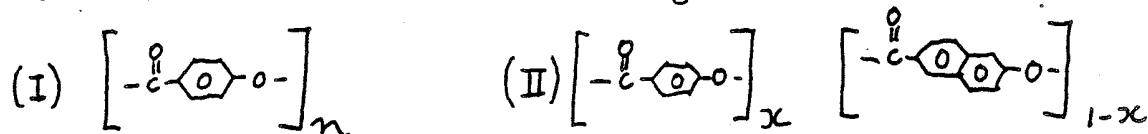
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ORDER IN THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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Rigid rod polymers typically have high melting points such that a mesophase can only be exposed by the addition of a solvent to give a lyotropic solution. In general, thermotropic polymers which are likely to have good mechanical properties will have semi rigid molecules, and their mesophase processibility can be enhanced through random copolymerization.

A study of poly hydroxy benzoic acid (I) and copolymers of the HBA unit with hydroxy naphthoic acid (II) has raised significant structural issues. In particular the nature of the homopolymer above its 350°C transition and the observation of optical biaxiality in the co-polymers, point to combinations of special local order with considerable chain mobility. The fact that the random copolymers can still show a crystal melting point is understood in terms of a model defining lateral order between random sequences.



"RHEOLOGICAL ASPECTS OF THE PROCESSING OF
NEMATIC POLYMER SOLUTIONS"

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Nematic polymer solutions exhibit substantially different rheological properties from their isotropic counterparts. Studies on nematogenic solutions of the rodlike chain poly(1, 4 -phenylene -2, 6- benzobisthiazole), PBT, will be discussed to illustrate these differences. Comparisons of the viscous behavior in slow flow with that predicted with use of the Leslie-Ericksen constitutive equations will be given, along with comparison of viscoelastic behavior observed in more rapid flows with the behavior predicted with a single integral constitutive equation. Implications for memory effects and flow instabilities will be considered, along with remarks on the effects of these on certain types of solution processing. Finally, apparent deficiencies in models currently available to represent the rheological properties of nematic polymer solutions will be discussed.

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DEVELOPMENT OF ORDER IN PROCESSING FLEXIBLE POLYMERS. A. Ziabicki,
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High degree of chain extension, crystallinity and orientation in polymers composed of flexible chains require that high stress is applied to the boundary of the sample and uniformly transmitted to individual macromolecules. Non-linear stress-orientation characteristics and the effects of orientation on crystal nucleation are analyzed and discussed.

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STIFF CHAIN HETEROCYCLIC POLYMERS. James F. Wolfe, Polymer Chemistry, SRI International, 333 Ravenswood Avenue Menlo Park, CA 94025

This lecture traces the development of a class of stiff chain, aromatic heterocyclic polymers (called PBZ) based on benzothiazole or benzoxazole ring structures that form thermooxidatively stable, high strength, high modulus fibers and films. A new process for polymerizing in poly(phosphoric acid) (PPA), in which the phosphorus pentoxide content of the PPA is adjusted to account for the higher concentration of condensing species in the concentrated solutions, has led to high molecular weight, rigid-rod and extended-chain structures that form lyotropic liquid crystalline reaction mixtures at polymer concentrations between 5 and 20 wt %. These PPA/PBZ reaction mixtures can be processed directly into highly ordered, crystalline morphologies, by techniques such as dry-jet wet-spinning. Tensile strengths of 400,000 to 700,000 psi with tensile moduli of 15 to 70 million psi combined with densities of 1.5-1.6 g/cc, excellent hydrolytic, thermal, and UV stability make these polymers strong candidates for many applications where performance/weight is important, such as reinforcements for composites, protective clothing and high performance tire cord, fabrics and cables.

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IMPROVEMENTS IN THE PROPERTIES OF PAN-BASED CARBON FIBRES. C.F. Holleyman,
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Over the last eight years the worldwide market for carbon fibre has increased by some 1,500%. From initial usage in sports goods, carbon fibre composites are now finding increasing usage in major aerospace programmes. This has led to increasing pressure from aircraft designers calling for enhanced composite performance which has prompted major research into improving carbon fibre properties:

Against a background of a 50% improvement in fibre strength across the period 1971 - 84 this paper will outline more recent R & D effort directed at further improving the properties of the Hysol Grafil range of fibres. This has concentrated on reducing levels of particulate contamination and improving the fibre crystal structure. Combined efforts in these areas have led to the launch of a new product range with fibres having strengths, at 750 ksi, well over twice the levels originally attained in 1971.

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THE MESOPHASE IN CARBONACEOUS PITCHES. L.S. Singer*, Union Carbide Corporation, Carbon Products Division, Parma Technical Center, P.O. Box 6116, Cleveland, Ohio 44101.

The thermal transformation of most organic materials to carbon and graphite proceeds through an intermediate mesophase pitch, a nematic liquid crystal consisting primarily of disc-like molecules. Recent phase separation studies indicate a remarkable similarity of the constitution of the coexisting isotropic and anisotropic phases. The response of the unique liquid crystal phase to mechanical stresses and magnetic fields is of particular importance in understanding the preferred orientation, high stiffness, and strength of certain derived carbon fibers and other carbon and graphite products. The characterization by EPR and ENDOR of the free radical intermediates in these thermally-treated pitches and their fractions has also helped to clarify the mechanisms of the thermal polymerization and carbonization reactions.

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POLYMER SINGLE CRYSTAL FIBERS. R. J. Young, Department of Polymer Science and Technology, UMIST, P.O. Box 88, Manchester. M60 1QD, U.K.

This presentation is concerned with the development of polymer single crystal fibers as high strength reinforcing fibers for applications such as in polymer-matrix composites. It is found that polydiacetylene single crystal fibers made by the solid-state polymerisation of single crystal monomers have high degrees of strength and stiffness and are inherently resistant to creep. It will be shown that investigations upon these materials have led to significant improvements in our understanding of fundamental structure/property relationships in polymers and have enabled the theoretical strengths of polymer molecules to be determined. Measurements upon the deformation of model polydiacetylene/epoxy composites have enabled the micromechanics of fibre reinforcement to be studied in detail. The findings of this present study are being extended and expanded to cover the behaviour of other high modulus polymer fibers such as Kevlar.

P. L. Lemstra

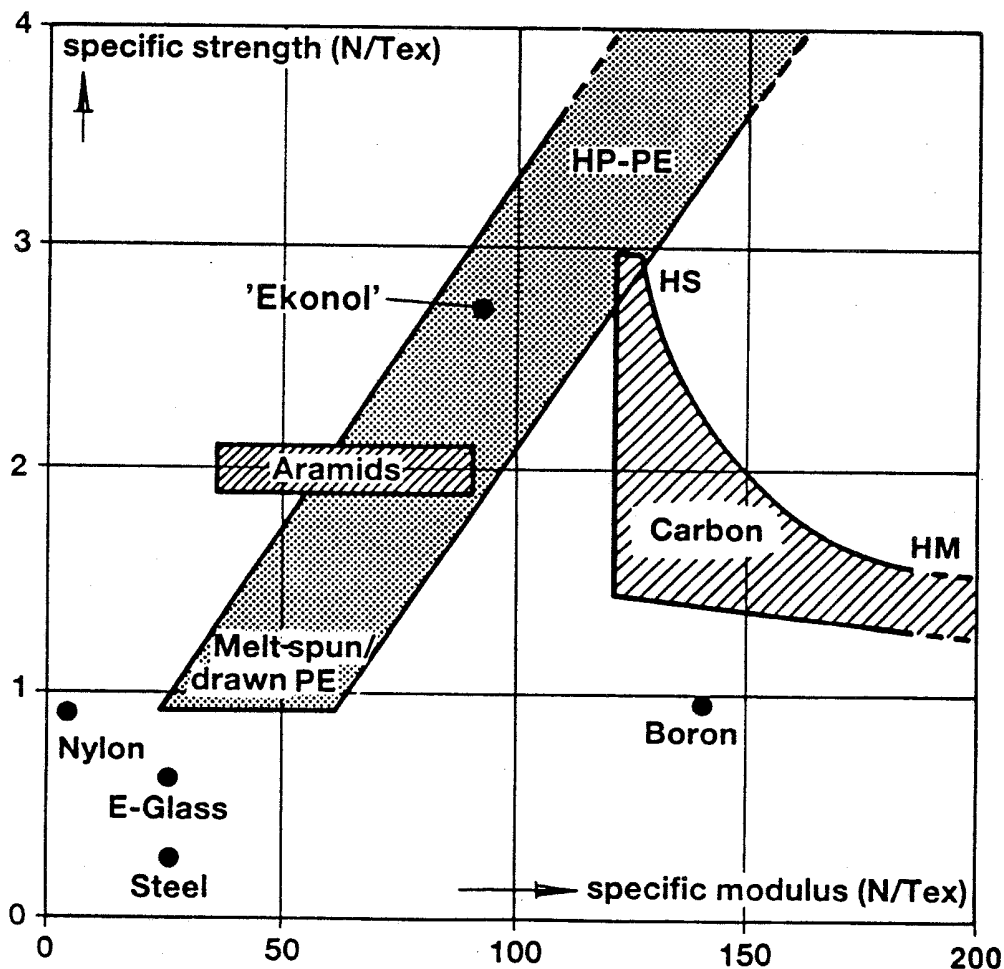
Technical University of Eindhoven, The Netherlands

High-Strength/High-Modulus Structures from Flexible Macromolecules

During the past ten years great progress has been made towards the development of high-strength/high-modulus structures based on flexible macromolecules. Amongst the various methods which have been developed, solution-spinning/drawing of ultra-high-molecular-weight polyethylene (UHMW-PE) proved to be most versatile. The basic principles of this process, now often referred to as gelspinning, were established during the late seventies at DSM-Research.

Currently, chain-extended polyethylene fibres are being produced continuously which compete, in terms of specific strength and stiffness, with aramid and carbon fibres, see diagram below: HP-PE = high-performance polyethylene. The polymer concentration in solution is a paramount factor with respect to the ultimate properties (strength, modulus, creep) of HP-PE fibres. Currently, a wide concentration range of UHMW-PE solutions can be processed resulting in the possibility to produce a spectrum of HP-PE products including fibres, tapes and films.

Although polyethylene featured as the prime candidate in developments concerning high-strength/high-modulus chain-extended flexible polymers, other systems have been examined and promising results were obtained. The limiting properties of chain-extended flexible polymers in relation to processing conditions and molecular characteristics will be discussed.



ARAMID COPOLYMER FIBERS RELATED TO TECHNORA^{T.M.}. S. Ozawa, Central Research Laboratories, Teijin Limited, Hino, Tokyo, JAPAN 197

A 50:50 copolymer of terephthalamides of *p*-phenylenediamine and 3,4'-diaminodiphenyl ether were prepared by the solution polycondensation in N-methylpyrrolidone to give a homogeneous spin dope. Extremely strong and tough fibers were obtained by a dry-jet wet spinning of the dope and by subsequent super-drawing of the raw fiber. The fiber exhibited various interesting and useful properties other than very high tenacity (25 g/d) and tensile modulus (570 g/d): unusual resistance against strong acids and alkalis as well as even oxidizing and reducing agents, rather low specific weight (1.39), rather high elongation (4%) at break, etc. The fibers can be used as tension members for various applications, also as reinforcement fibers for not only rubber and plastics, but also for concrete, and of course as textile fibers for protective garments against both heat and cut.

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THERMOTROPIC MELT FIBERS - ULTIMATE PROPERTIES BY HEAT STRENGTHENING.
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Ultimate properties of fibers spun from thermotropic melts are achieved by the process of heat strengthening. Lower molecular weight aromatic polyesters and polyazomethines are spun from thermotropic melts to produce well oriented moderately strong fibers. These latter are heated in a relaxed state for seconds to hours while being purged with an inert gas at temperatures below the fiber flow temperature to produce significant increases in fiber tenacity. The extent of property enhancement and the changes in structure and molecular weight accompanying the process as well as the effect of polymer composition and catalysts on rate and degree of heat strengthening will be discussed.