First European Tri-Service Advanced Materials Workshop

COMPRESSIVE STRENGTH IN RIGID-ROD POLYMERS

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Pembroke College
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PREFACE

The First European Tri-Service Advanced Materials Workshop: Compressive Strength in Rigid-Rod Polymers is held at Pembroke College, University of Cambridge, September 3-5, 1992. The Workshop brings together a small and select group of experts in the Physics, Engineering, Chemistry, and Materials aspects of compressive problems in these polymers. The abstracts which follow reflect the lectures by the distinguished scientists at the Workshop. It is the intent that as a result of intensive discussion concerning origins and manifestations of compressive failure in rigid-rod polymer systems, rational approaches for solving these problems may arise.

We wish to acknowledge the following organizations for support of the Workshop: USAF European Office of Aerospace Research and Development; US Army Research, Development and Standardization Group, UK; Office of Naval Research European Office.

Anselm C Griffin
Melville Laboratory for Polymer Synthesis
University of Cambridge
27 August 1992

Improvement of compressional strength in rod-like polymers: synthetic approaches and morphological studies

G. Wegner, G. Lieser, Wei Wang, R. Zierer and V. Enkelmann
MPI für Polymerforschung, Mainz, Germany

Abstract

A series of n-alkyl substituted homo- and copolymers of poly-p-phenylene terephthalamid with the alkyl groups attached to the diamine, diacid or to both moieties have been synthesized. The hypothesis was that the alkyl groups would induce packing defects (Disclinations) which in turn would help to dissipate local stress when fibres of the polyaramid are loaded under compression. The crystal structure of the appropriate oligomers was determined in order to develop a picture of how the n-alkyl side groups affect the packing conditions of the backbone units.

The phase diagram of the copolymers in conc. sulfuric acid was determined and influences of the side groups on the existence range of the l.c. phase were quantitatively evaluated. Fibres have been spun from the l.c. phase which gave reasonable to good values of the Youngs modulus but failed to demonstrate a significant improvement in compressional strength.

Furthermore, phenomena of chain segregation according to length when rigid-chain macromolecules are crystallized from the l.c. phase have been investigated using a particular polydiacetylene as a model polymer. Features completely akin to morphological phenomena observed in polyaramid fibres were seen. They can be rigorously assigned to textures commonly seen in l.c. phases and details of the chain arrangement could be resolved. The most significant effect is a segregation according to chain length in the equilibrium morphological structure. The formation of shear bands is a transient phenomenon in the course of the system towards equilibrium textures.

THE COMPRESSIVE YIELD BEHAVIOUR OF POLYBENZIMIDAZOLE

I. M. WARD.

IRC in Polymer Science and Technology.
University of Leeds, LEEDS LS2 9JT

Polybenzimidazole (PBI) is a rigid polymer with a Young's modulus of 6 GPa and a remarkably high compressive strength of 400 MPa at room temperature. It is also hydrophilic and absorbs 15% by weight of water at room temperature at 100% relative humidity, which reduces the compressive strength by about a factor of two.

Recent research at Leeds University (1) has involved measurements of the mechanical behaviour of PBI over a wide range of temperatures, together with more limited studies of strain rate dependence. Two issues have been particularly addressed

(1) Is the yield process in PBI different in kind from the yield process of more conventional polymers such as polyethylene or polymethylmethacrylate?

(2) What is the role of water in affecting the mechanical behaviour of PBI, and does structural information from infra red, Raman and NMR provide insight on this question?

REFERENCES

(1) J.D.Rose, R.A.Duckett and I.M.Ward (to be published).

Compressive Strength Improvements in Rigid-Rod Polymeric Fibers - A DuPont Perspective

S. R. Allen
Advanced Fibers Systems
E. I. duPont deNemours & Co., Inc.
Richmond, VA

Compressive strengths of high modulus/high strength organic fibers are, in general, much lower than those of their counterpart reinforcing fibers based on metals, ceramics and graphite/carbon. A tremendous amount of effort has been focused over the last few decades in both industrial and university research laboratories towards the characterization, understanding and improvement of the compressive strength of these organic based reinforcing fibers. A wide range of characterization methodologies have been evolved to evaluate compressive properties, both for individual fibers as well as for reinforced composites based on them. Numerous organic based reinforcing fibers have been explored in the search for understanding and improvement. Synthetic approaches have also focused on a variety of schemes to impart crosslinking via thermal, chemical and ionic chemistries in order to enhance intermolecular and interstructural interactions. Various systems approaches to enhance the structure and morphology of the fibers have been explored such as surface treatments, co-spun additives, imbibition, and coatings. This presentation will serve to review such efforts explored in DuPont research as a basis for discussion at the workshop.

FACTORS AFFECTING COMPRESSIVE PROPERTIES OF HIGH PERFORMANCE COMPOSITES

by

James Economy
University of Illinois at Urbana-Champaign
Urbana, Illinois

Approximately two years ago, we initiated a program with DARPA/ONR support to develop possible approaches to resolving the above problem. Initially we looked at the respective roles of the fiber, interface and matrix. With respect to the fiber, we were interested in evaluating the role of the microfibrillar morphology in many of the candidate fibers and also in designing and evaluating reinforcing agents which do not have a microfibrillar morphology. We also undertook to assess the current approach to oxidizing the carbon fiber surface to enhance bonding to the matrix. Finally, we decided to develop a new kind of matrix system based on aromatic liquid crystalline copolyesters to take advantage of the much higher modulus of such systems (presumably 2 to 3 times of epoxy). In this presentation progress in all three areas is smmarized. Particular emphasis is placed on the areas of the reinforcing agents and the matrix.

Abstract:

THE RELATION BETWEEN INTERMOLECULAR FORCES AND THE COMPRESSIVE STRENGTH OF REINFORCING FIBRES

M.G. Northolt

Akzo Research Laboratories Arnhem, Corporate Research, P.O. Box 9300,
6800 SB Arnhem, The Netherlands.

The range of compressive strength values observed for the various kinds of polymer fibres seem to indicate that the interchain forces together with the chain rigidity determine to a large extent this fibre property. The shear failure mechanism as manifested by the formation of kinkbands at compressive failure of reinforcing fibres, including carbon fibres, provides further support for the important role of the intermolecular forces. Therefore it seems likely that the only way to increase the compressive strength of polymer fibres will be to introduce covalent crosslinks. This hypothesis view will be illustrated by a discussion of the results of a study of the tensile and compressive behaviour of pitch-based and PAN-based carbon fibres.

ABSTRACT

SYNTHETIC EFFORTS FOR IMPROVED COMPRESSIVE PROPERTIES OF RIGID-ROD POLYMERS

AIR FORCE WRIGHT LABORATORY
MATERIALS DIRECTORATE, POLYMER BRANCH
WRIGHT-PATTERSON AFB, OHIO 45433

Considerable research efforts in recent years have been directed toward the synthesis, characterization and fabrication of benzobisazole rigid-rod, polymers. These systems have exhibited excellent high strength, high-modulus values with superior thermal and thermaloxidative properties as compared to the state-of-the-art. Modulus values of 50-60 msi, with tensile strength of 500 ksi have been obtained on fibers after heat treatment. Although these fibers exhibit excellent mechanical properties, they suffer from relatively low axial compressive strength (50 ksi). A number of structural modifications on benzobisazole polymer systems have been carried out in our laboratory. The presentation will be focused on those structural variations made by maintaining the para-ordered rigid-rod geometry while modifying the structure with pendent groups. Model polymer systems were prepared and evaluated to test an increase in lateral order, disrupting packing order, chemical crosslinking and ribbon-like morphologies.

SAXS STUDIES OF MICROVOIDS IN HIGH MODULUS FIBERS

W. Ruland

Dept. of Physical Chemistry and Center for Materials Science
University of Marburg, Germany

Carbon fibers and PPTA fibers show a small-angle scattering which is due to microvoids with highly anisotropic shapes. The microvoids are preferentially oriented with the largest dimension in the direction of the fiber axis. The result is a fan-shaped intensity distribution with maximum intensity on the equator. In addition to the scattering of microvoids, there is an intensity component due to the density fluctuation within the compact material.

Two types of SAXS measurements are carried out. 2D intensity distributions are obtained on photo film by pin-hole collimation. Plots of the angular width of the fan-shaped intensity distribution as a function of the distance from the origin of reciprocal space lead to the determination of an orientation parameter and the average size of the largest dimension of the microvoids. Measurements with slit collimation are performed with the slit parallel to the fiber axis resulting in a projection of the 2D intensity distribution onto the plane perpendicular to the fiber axis. This permits the determination of the two other dimensions of the microvoids, the segment length in the cross section, the density fluctuation and, by absolute intensity measurements, the volume content of microvoids.

Carbon fibers produced from mesophase pitch have disk-shaped microvoids whereas PAN-based and rayon-based carbon fibers as well as PPTA fibers have ribbon-shaped microvoids. The largest dimension is in the range of 100 Å to 900 Å, the shortest in the range of 10 Å to 30 Å. The density fluctuations are 1D in carbon fibers and 2D in PPTA fibers. Porod's law is valid for large scattering angles in all cases, *i.e.*, the walls of the microvoids are smooth, the surface fractal dimension is 2.

Abstract *for 1st European Tri-Service Advanced Materials Workshop: "Compressive Strength in Rigid-Rod Polymers", Cambridge, England, Sept. 3 - 5, 1992*

PBO FIBER COMPRESSIVE STRENGTH

J. Im, C. C. Chau, M. Vedula and N. L. Madison
The Dow Chemical Company
Central Research & Development
Midland, Michigan 48674, USA

Compression behavior of poly(phenylene-benzobisoxazole) PBO fiber was studied using SEM and TEM. Fiber compression induced localized kinks, having a uniform thickness and distinct boundaries separating the kinked and unkinked regions. The localized kinks were 45 nm thick with a constant shear strain, 0.7 along the kink and had an orientation of 67° from the fiber axis. A mutual shearing effect seemed to occur at the kink intersections, in which the fibrils were reoriented to a new direction determined by shear displacement of the individual intersecting kinks. These observations indicate that kink bands were initially formed by shear motion.

Various approaches; chemical, mechanical and composite in nature, were taken to improve compressive strength of PBO fiber. These approaches will be illustrated, together with the resulting compressive strengths. The measurement of compressive strength was performed mainly by employing a 'minicomposite' method for chemical and mechanical approaches, then an (ASTM) composite method for the composite approaches. The test methods and the associated fiber failure modes will be discussed.

A MECHANISM FOR COMPRESSIVE FAILURE IN AROMATIC POLYAMIDE FIBRES

by

D. LU AND R. J. YOUNG

Polymer Science and Technology Group

Manchester Materials Science Centre

UMIST/University of Manchester

Manchester M1 7HS, UK

ABSTRACT

The compressive properties of a number of well-characterised aromatic polyamide (aramid) fibres have been studied using a combination of optical microscopy and Raman spectroscopy on a single-fibre model composite. The effect of the tensile modulus upon the compressive behaviour of aramid fibres has been investigated and it has been found that there is an inverse relationship between the strain for the onset of visible kink band formation and the tensile modulus of the fibres. The fibres with the highest tensile modulus require the lowest strain for kink band formation. Raman spectroscopy has been used to follow the full tension-compression stress/strain relationships for the fibres. Using the measured relationship between fibre modulus and Raman band shift it has been possible to estimate the compressive moduli of the fibres. It is found that the lower modulus fibres have a higher modulus in compression than in tension whereas the reverse is the case for fibres with a higher tensile modulus. It is then found that the compressive failure stress of the fibres increases with increasing compressive modulus and this is consistent with the failure mechanism of the fibres being a simple *Euler Buckling* process.

Molecular Dynamics Computer Simulation Strategies for Investigating Surface Buckling and Compressive Strength

R. Hentschke, Max-Planck-Institut für Polymerforschung, Postfach
3148, 6500 Mainz, Germany

It is probably a fair statement that the microscopic effects leading to failure under compressive loading of oriented polymers are insufficiently understood. The majority of models describing the formation of instabilities under compressive load are based either on single mechanical or persistent chains within an isotropic mean field due to neighboring chains or on continuum theories of elastic instabilities. Whereas these models may successfully relate macroscopic moduli to compressive strength on a qualitative level, they exhibit a lack of quantitative predictive power for specific materials. This underscores the importance of a more detailed material oriented microscopic approach. Headway in this direction may come through the application of computer simulation techniques. In particular, the molecular dynamics technique, which can be used to describe the structure and dynamics of polymer systems down to the atomic scale, seems to be a promising tool for studying the initial stages of compressive failure in fibers of highly oriented polymers.

Here I will present a critical discussion of the contribution molecular dynamics simulations can make in this context, with an emphasis on the microscopic understanding of buckling processes as for instance encountered in the bending or peeling of strongly anisotropic polymer fibers. This includes different modeling strategies, which yield insight into microscopic structural and dynamic effects during compression, such as microscopic stress distribution or detailed information on the inter chain interactions. In addition, the spatial and temporal limitations of the method are discussed.

ORIENTATION OF RIGID-ROD POLYMERS IN SHEAR FLOWS

G. Marrucci
Department of Chemical Engineering, University of Naples
Piazzale Tecchio, 80125 Napoli, Italy

Prediction of molecular orientations in articles fabricated with liquid crystalline polymers (LCPs) still constitutes an open problem, especially when the fabricating process involves shear flows as in injection moulding rather than elongational flows as in fiber spinning.

One of the reasons might be the non-aligning (i.e., tumbling) character of LCPs which has been demonstrated, both theoretically and experimentally, in lyotropic rodlike LCPs and which, perhaps, is also to be expected in some semi-flexible thermotropic polymers.

A brief review of what is known today is here presented, the main points being the following ones:

1. Rigid rod-like polymers form a nematic phase which is of the tumbling type at small and moderate shear rates, to become flow-aligning at high shear rates as a result of nonlinearity.

2. Because of tumbling, defects and disclinations are likely to be generated which then relax very slowly. The defect density appears to be a function of shear rate and shear deformation.

3. Recent progress in the theory of defects indicates that, depending on their density and on shear rate, they can eventually stop the tumbling process. There exist indications, both theoretical and experimental, on the molecular orientation which is achieved under these conditions.

Phase Transformations and Microstructure Formation During Coagulation of Rigid-Rod Polymer Solutions.

Yachin Cohen, Department of Chemical Engineering,
Technion-Israel Institute of Technology, Haifa 32000, Israel.

High performance fibers and films are spun from solutions of rigid polymers in strong acids. The microstructure of these materials develops during the coagulation stage of the spinning process, when an oriented nematic solution of the rodlike polymer transforms to the crystalline state, under the action of a nonsolvent, typically water. Our research has centered on identifying the microstructure which forms during coagulation stage of the spinning process, in relation to the phase equilibria in the rigid-polymer/acid-solvent/waster-coagulant system. The motivation has been to identify the microstructural elements formed in the solidification stage and to seek kinetic pathways to control the microstructure in a way which may affect the compressive strength. We have studied the structure in in the wet-coagulated state of poly(p-phenylene benzobisthiazole) [PBZT] fibers spun from polyphosphoric acid [PPA] solutions. Microscopical observations together with x-ray scattering measurements revealed an interconnected network of oriented microfibrils, the width of which is less than 10nm. Is was proposed that collective buckling of the microfibrils is responsible for compressive failure. The transition to the crystalline polymer state is characterized by rapid kinetics due to deprotonatation of the polymer. It is thus of interest to study crystallization processes which do not involve deprotonation. We discovered two crystal-solvate forms in the PBZT/acid/water system, due to co-crystallization of polymer cations with acid anions. The conditions for the phase transitions, in terms of water concentration and temperature, have been evaluated. Slow coagulation using 85% phosphoric acid failed to alter the microfibril size, but enhanced the crystallite orientation and perfection. Microscopical observations suggest that the microfibrillar morphology develops in the transition from the ordered form I state to the less ordered form II state, and thus precedes the formation of the polymer crystals.

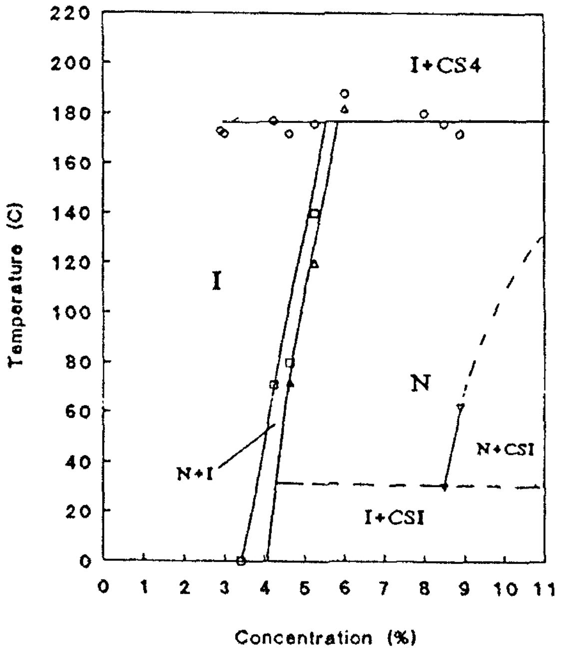
The Phase diagram of the system PBZT/PBO-P_2O_5-H_2O

H. Fischer, A. Keller and J. A. Odell

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue,
Bristol, BS8-1TL, U.K.

Recent work has highlighted the role played by the solvent in PBZT/PBO-PPA nematic solutions. The solvent may orient with the mesogens or else form crystal solvate phases. An understanding of the phase behaviour of such systems is therefore a prerequisite for enhancing our understanding of processing and morphology. The interest on the understanding of the phase behaviour of the liquid crystals PBZT and PBO in PPA solutions saw a focus on the construction of the binary and ternary phase diagrams of the system. Due the more or less complex phase behaviour of the solvent system PPA itself it was important to analyze the structure of the solvent in all investigated solutions. The method employed was ^{31}P-NMR spectroscopy. The phase diagram was constructed using polarization optical microscopy and DSC. A peritectic temperature at 180 °C was found, the temperature varied with the structure of the solvent. The formation of the crystal solvate at elevated temperatures is forced by the split off of water due to the condensation process of the PPA. The constitution of the orange-red crystal solvate (CS II) was found to be a composition of four phosphoric acid units per monomeric unit PBZT.

PHASE DIAGRAM PBZT-PPA



EFFECT OF MICROFIBRILLAR STRUCTURE ON COMPRESSIVE STRENGTH OF ULTRA-STRONG FIBERS

Dusan C. Prevorsek, Allied-Signal Inc. Morristown N.J. 07960 U.S.A.

The complex structure of high performance fibers has been the subject of numerous studies. It has been shown that almost all organic polymeric fibers exhibit well defined periodicity on micro (5 nM) and macro (50 nM) level. Simple mechanical considerations show that the dimension of the micro- and macro-fibrils, and the properties of the interfibrillar matter should play a much stronger role in the compressive strength of fibers than in their tensile properties.

It is also clear that the current data relative to the fibrillar structure are insufficient to carry out meaningful analyses. On the other hand, there is experimental evidence that the compressive properties can be affected by the processing conditions of fibers. It has also been observed that process modifications resulting in improved tensile properties frequently produce opposite effects on compressive strength.

To explain such data and develop background for a micromechanical analysis of compressive strength we undertook a study to determine the properties of the non-crystalline domains of ultra strong polyethylene. The methodology involves: 1) the characterization of fibers by Micro-Raman Microscopy that yields the strain distribution of the molecules in the crystalline phase, 2) the Wide- Angle X-ray diffraction from stressed samples that yields the strain distribution of the crystalline regions, 3) The micromechanical analysis based on the morphological data based on Small-Angle X-ray diffraction and Electron Microscopy that reproduces the shifts in X-ray diffraction patterns from stressed samples by varying the properties of the non-crystalline inter- and intra-fibrillar domains.

The structural model derived through this procedure that matches the tensile properties and morphological changes induced by tension is then used to calculate the properties in compression. Furthermore, the model allows us to systematically investigate the role of structural variables on the compressive strength and provides guidelines for process and polymer modifications. The calculations explain a great deal of experimental data and the methodology is applicable to all types of organic polymeric fibers.

Towards the Design of Non-Mesogenic Rigid Rod Polymers

Chaobin He, A. C. Griffin, and A. H. Windle

Melville Laboratory and Department of Materials Science,
Pembroke Street,
Cambridge,
CB2 3QZ, UK

The intrinsic tendency of rigid rod polymers to mutually align, leads one to view them as the natural route to the achievement of high tensile fibres, as indeed they are. It is because of the concomitantly poor properties of fibres in non-axial directions, and indeed in compression along the fibre axis, that we have taken another approach. The objective has been to design rigid rod molecules which do not align parallel to form mesophases. The approach is based on the synthesis of 2,2',6,6' tetra substituted biphenyl groups para linked into the chains. Where the substituted groups are large, the chain will in effect have lumps along its length which should frustrate parallelism. Exploratory syntheses using substituted groups up to phenyl esters in size, have shown that a family of polymer glasses can be created which:

(i) show neither crystallinity nor thermotropic liquid crystallinity
(ii) have high glass transition temperatures
(iii) show remarkable solubility in some cases in modest solvents such as DMF .

Initial structural studies of the new polymers confirm the random packing of the chains, while conformational analysis demonstrates the enhancement of chain rigidity by the substituted groups.

NOTES