HIGH MODULUS POLYMERS AND COMPOSITES

Lectures at the
1984 International Summer School
at The Chinese University of Hong Kong
16-26 July 1984

Roger S. Porter Motowo Takayanagi
James Economy Bryan Harris

Edited by C. L. Choy

The Chinese University Press
Hong Kong

International Standard Book Number: 962-201-331-7

The Chinese University Press
The Chinese University of Hong Kong
SHATIN, N.T., HONG KONG

Printing by Caritas Printing Training Centre, Hong Kong

ADVISORY COMMITTEE

B. HSU	The Chinese University of Hong Kong
Y. C. HU	Academia Sinica
Y. W. LAM	The Chinese University of Hong Kong
T.C.W. MAK	The Chinese University of Hong Kong
R. S. PORTER	University of Massachusetts
R. Y. QIAN	Institute of Chemistry, Academia Sinica
M. TAKAYANAGI	Kyushu Sangyo University
I. M. WARD	University of Leeds

ORGANIZING COMMITTEE

Chairman

R. S. PORTER	University of Massachusetts

Members

E.S.W. KONG	Sandia Laboratories
S. H. KWAN	Hong Kong Polytechnic
W. P. LEUNG	The Chinese University of Hong Kong
H. C. NG	The Chinese University of Hong Kong
Y. H. ZHU	Academia Sinica

Secretary

C. L. CHOY	The Chinese University of Hong Kong

PARTICIPANTS

ASUNDI, Anand	University of Hong Kong
AU, Tak Yan	Hong Kong Polytechnic
BAHRI, Randhir	Punjabi University, India
CAI, Weizhen	Institute of Chemistry, Academia Sinica
CHAN, Wah On	Hong Kong Polytechnic
CHAN, Wing Hong	Hong Kong Baptist College
CHEN, Chihchuan	South China Institute of Technology, Guangzhou
CHEN, Mingchai	Guangzhou Institute of Chemistry, Academia Sinica
CHEN, Yuping	Institute of Chemistry, Academia Sinica
CHOW, Kim Fung	The Chinese University of Hong Kong
CHOW, W. S.	University of Cincinnati, USA
CHOY, Chung Loong	The Chinese University of Hong Kong
CHU, Ka Fu	Hong Kong Polytechnic
COVAVISARUCH, Sirijutaratana	Chulalongkorn University, Thailand
DAI, Fuling	Institute of Mechanics, Academia Sinica
DAS, Bibekananda	University College of Science and Technology, India
DING, Dawen	Feng-Chia University, Taiwan
DU, Qiangguo	Fudan University, Shanghai
GHARIANI, Krayem Abd-El-Hadi	National Taiwan University, Taipei
GUO, Meili	Beijing Institute of Astronautics
GUPTA, Avadhesh Kumar	Indian Institute of Technology, New Dehli
GUPTA, Moolchand	Nagpur University, India
HE, Jiasong	Institute of Chemistry, Academia Sinica
HE, Pingsheng	University of Science and Technology of China, Hefei
HE, Tianbai	Changchun Institute of Applied Chemistry, Academia Sinica
HE, Yuankang	Peking University, Beijing
HEMACHANDRA, Khemchai	Chulalongkorn University, Thailand
HO, Guoren	Zhongshan University, Guangzhou
HO, Kam Ho	The Chinese University of Hong Kong
HONG, Michael K. M.	University of Hong Kong
HONG, Wei	Qinghua University, Beijing
HU, Fuzeng	East China Institute of Chemical Technology, Shanghai

HUQUE, Monimul	Bangladesh University of Engineering and Technology, Dhaka
LEE, Shu Leung	The Chinese University of Hong Kong
LEE, Wing Bun	Hong Kong Polytechnic
LEE, Yew Wing	Hong Kong Polytechnic
LEUNG, Wing Pun	The Chinese University of Hong Kong
LI, Jibo	South China Institute of Technology, Guangzhou
LIU, Biqian	Institute of Chemistry, Academia Sinica
LIU, Yunqi	Institute of Chemistry, Academia Sinica
LO, Hing Yan	Dow Chemical (Hong Kong) Ltd
LO, Yuk Ming	The Chinese University of Hong Kong
LONG, Chengfen	Institute of Chemistry, Academia Sinica
LU, Sinien	Institute of Mechanics, Academia Sinica
LU, Zhonghe	Guangzhou Institute of Chemistry, Academia Sinica
MANNAN, Kh. A.I.F.M.	Dhaka University, Bangladesh
McCALL, Colin	Hong Kong Polytechnic
NG, Howard C.	The Chinese University of Hong Kong
ONG, Eng Lian	The Chinese University of Hong Kong
QI, Zhongneng	Institute of Chemistry, Academia Sinica
QIAN, Renyuan	Institute of Chemistry, Academia Sinica
SASHI KUMAR, Kunnath	Asian Institute of Technology, Thailand
SHEN, Wei	Huazhong University of Science and Technology, Wuhan
SHIN, Franklin George	Hong Kong Polytechnic
SISWANTO, Muliawati	University of Indonesia, Jakarta
TEE, Tiam Ting	University of Malaya, Kuala Lumpur
TEH, Joo Wooi	Science University of Malaysia, Pulau Pinang
TSUI, Wan Lam	Hong Kong Polytechnic
WANG, Huei Hsiung	Feng-Chia University, Taiwan
WANG, Lihui	Fudan University, Shanghai
WANG, Xiayu	Xiangtan University, Hunan
WONG, K. H.	The Chinese University of Hong Kong
WONG, Pak Yeung	The Chinese University of Hong Kong
WONG, Sai Peng	The Chinese University of Hong Kong
WU, Renje	Institute of Chemistry, Academia Sinica
WU, Xiaohua	South China Institute of Technology, Guangzhou
XIA, Yuanming	University of Science and Technology of China, Hefei
XIE, Ping	Institute of Chemistry, Academia Sinica

XU, Changhua	Institute of Chemistry, Academia Sinica
YIP, Hon Wai	Dow Chemical (Hong Kong) Ltd
YOUNG, Kenneth	The Chinese University of Hong Kong
YUE, Chee Yoon	University of Hong Kong
ZHANG, Anqiu	East China Institute of Textile Science and Technology, Shanghai
ZHENG, Weiping	Institute of Mechanics, Academia Sinica
ZHENG, Yongchang	South China Institute of Technology, Guangzhou
ZHENG, Zhizhuang	Polymer Aging Research Institute, Guangzhou
ZHU, Xiaoguang	Institute of Chemistry, Academia Sinica

OPENING ADDRESS

Professor Baysung Hsu
Acting Vice-Chancellor
The Chinese University of Hong Kong

I am most happy to welcome you to this International Summer School on High Modulus Polymers and Composites.

This is the Second International Summer School organized by The Chinese University of Hong Kong to help promoting the transfer of scientific knowledge and technological innovation to the developing regions of Asia. High Modulus Polymers and Composites is an area of research which has gained in importance in recent years, caused by the increasing use of polymeric materials and composites in industry and everyday life. This topic therefore blends basic scientific investigation with technological developments. We are indeed fortunate to have as lecturers in this School four scientists who are prominent in this field.

This School is directed by Professor Roger S. Porter, Co-Director of Materials Research Laboratory at the University of Massachusetts. The other lecturers are Dr. Motowo Takayanagi, Professor of Industrial Chemistry at Kyushu Sangyo University; Dr. James Economy, Manager of Organic and Polymer Research at IBM San Jose Research Laboratory and Professor Bryan Harris, Head of School of Materials Science at University of Bath. We are grateful that they have taken time out of their busy schedule to participate in this event.

This Summer School is financed largely by the Croucher Foundation of Hong Kong. IBM has provided travel expenses for one of the lecturers, Dr. James Economy. Many participants are sponsored by UNESCO, Shell (H.K.), Dow Chemical (Asia Pacific) and CIBA-GEIGY (H.K.) The Asian Physics Education Network of UNESCO and Asian Physical Society are co-operative bodies to the School. I would like to take this opportunity to thank all these organizations for their support.

The programme of the Summer School is very intense. It is packed with lectures and seminars with very little time off. You will all be very busy in the next ten or eleven days. But I am sure that you will benefit greatly from taking part in the School. I wish you every success.

TABLE OF CONTENTS

HIGH MODULUS POLYMERS FROM FLEXIBLE CHAIN THERMOPLASTICS

Roger S. Porter
Department of Polymer Science & Engineering
Materials Research Laboratory
University of Massachusetts, Amherst, MA 01003 USA

ABSTRACT

A review is provided for the field of high modulus fibers. Emphasis is placed on research for the development of high tensile moduli from flexible chain polymers, with polyethylene used as an example. Advances in drawing techniques and in the characterization of draw are also reviewed. These developments with flexible chain polymers are compared to the recent U.S. advances in the achievement of high modulus fibers from rigid rod polymers.

TABLE OF CONTENTS

1. RECENT DEVELOPMENTS IN HIGH MODULUS POLYMERS

A. Perspective

The world position of nations is currently influenced by technology. In this contemporary competition, the science and engineering of materials is critical.

With the competition over steel an established example, we may consider the prospects for the two other major classes of materials, ceramics and polymers. The latter class of materials, polymers, is also being challenged in Japan. The following stark example is an excerpt from a translation of "Nikkei Sangyo Shimbrun, 7/27/82".

The Ministry of International Trade and Industry (MITI), the synthetic fiber industry, and academic institutions are to engage in the joint development and practical application of "the third generation fiber" which will have more than twice the high tenacity, high modulus, low elongation and other properties of the present fibers. MITI has designated as a government subsidized project, effective fiscal year 1983, this next generation research/development program. The industrial infrastructure plans to allocate 3 billion - 5 billion yen in funds with practical application targeted at five years in the future. The new fiber is expected to replace nylon and carbon fiber and expand the area of fiber demand. MITI and the industry, therefore, look forward to the contribution of this development project as a conclusive factor for the revitalization of the fiber industry now suffering from the structural recession, and for increasing the product value-addition.

At present, the closest fiber to this third generation fiber is DuPont's Aramid (also known as "Kevlar®-49"), with a high tenacity of ~ 28 grams/denier ~ 3.6 GPa, the world's most tenacious (commercial), but with a maximum modulus inferior to carbon fiber and polyethylene.

This is the world's first development project in the area of new materials, which is of equal importance with electronics

and biotechnology. It is particularly uniquely Japanese, because the research project is to be conducted jointly by government, industry and academic circles under the government subsidy program.

B. Flexible Polymers, the Polyethylene Example

Polymer researchers have approached the problem of making the strongest possible polymers in two diverse ways: (1) by chemically constructing polymers with rigid and linear backbone chains and (2) by processing existing conventional polymers in ways that a permanent transformation of the internal structure and properties occurs. Chemical construction of rigid macromolecules has been approached by syntheses leading to para-substituted aromatic rings in the polymer backbone. In general, these polymers cannot be processed by means of the common polymer-processing techniques; however, some industrial examples, viz, Kevlar and X-500, have been processed into fibers (of very high strength).

In the second category, polymers are converted into a highly oriented chain conformation with substantially increased modulus by drawing from a dilute flowing solution, gel state, or by extruding a supercooled melt, or by solid-state extruding or drawing below the melting point under controlled conditions.

New and successful drawing techniques have been recently developed by workers in the U.S. (at UMass) and Japan. It has been found possible to ultradraw single crystal mats of ultrahigh molecular weight polyethylene (UHMWPE). By the principal deformation technique of solid state coextrusion, draw has been achieved even at room temperature, and at up to 130°C, i.e. to below the melting point. Moreover, a stable extrudate results which exhibits a high crystal orientation. Multiple drawing by repeated coextrusion at 110°C produced an extrudate of UHMWPE with a draw ratio (DR) of 110 and a tensile modulus of 100 GPa. An even higher DR was achieved by a combination of solid-state coextrusion followed by tensile drawing at controlled rate and

temperature. The maximum achieved for the present by this drawing combination was a DR of 250. This superdrawn sample gave a tensile modulus of 222 GPa. This is about twice the highest previously reported room temperature experimental value (110 GPa) for polyethylene. Figure 1 summarizes these new results and provide a comparison with previous achievements by solid state drawing of high density polyethylenes.

C. Rigid-Rod Polymers

Various molecular architectures and processing procedures have been employed to achieve high modulus and high strength in polymeric fibers. Linear, flexible chain polymers, semi-rigid chain polymers and extended or rigid chain polymers all have been manufactured into fibers with high tensile mechanical properties. Additionally, carbon and graphitic fibers produced from polymeric precursors exhibit some of the highest performance characteristics of commercially available materials to date.

Carbon and graphitic fibers have been extensively investigated over the last two decades owing to their high temperature stability and exceptional mechanical properties. Commercially available fibers possess tensile moduli of up to 690 GPa along with tensile strengths of 2.2 GPa [7]. While such fibers have amply demonstrated high tensile modulus and strength, they are quite brittle which may limit their use in various applications. Also in order to produce carbon and graphitic fibers extreme processing conditions are required resulting in high production costs and hence final material cost. Additionally, the high electrical conductivity of these fibers is not always desired in high performance applications. While carbon fibers have demonstrated very desirable high performance characteristics there still exists a need for other high performance materials. Work on new materials is continuing in many areas and a sizeable amount of this activity is concerned with extended chain or rigid rod polymers possessing high performance characteristics.

Fibers produced from lyotropic liquid crystalline solutions of extended chain polymers have not only achieved desirable high performance characteristics but have become commercially successful engineering materials through the development of conventional wet spinning techniques for their manufacture. Both Monsanto [8] and duPont [9] have had success in developing high modulus/high strength fibers based on wholly aromatic polymers which possess a rod-like character deriving from steric effects; however, only duPont has pursued commercial development (Kevlar®). This success in producing high performance fibers from extended chain macromolecules has encouraged further investigation of rigid rod polymers. A sizeable research effort sponsored by the U.S. Air Force Wright-Patterson Materials Laboratory and the U.S. Air Force Office of Scientific Research (Ordered Polymers Research Program) [10] is currently investigating the high performance nature of novel rigid macromolecules.

REFERENCES

1. Polymer Science and Engineering: Challenges, Needs and Opportunities Report of the Ad Hoc Panel on Polymer Science and Engineering, National Research Council (1981).
2. Organic Polymer Characterization, NMAB 332, National Materials Advisory Board (1977).
3. Polymer Materials Basic Research Needs for Energy Applications, CONF-780643, U.S. Department of Energy (1978).
4. Workshop Proceedings: Morphology of Polyethylene and Cross-Linked Polyethylene, EPRI EL-2134-LD (1981).
5. Organic Matrix Structure Composites: Quality Assurance and Reproducibility, NMAB-365, National Materials Advisory Board (1981).
6. Materials for Lightweight Military Combat Vehicles, NMAB-396, National Materials Advisory Board (1982).
7. W. Bruce Black, "High Modulus/High Strength Organic Fibers", Ann. Rev. Mater. Sci., 10, 311 (1980).

8. W.B. Black and J. Preston, editors, High Modulus Wholly Aromatic Fibers, Marcel Dekker, New York (1973).

9. H. Blades, U.S. Patent 3,869,430, "High Modulus, High Tenacity Poly(p-Phenylene Terephthalamide) Fiber", assigned to duPont (1975).

10. T.E. Helminiak, "The Air Force Ordered Polymers Research Program: An Overview", A.C.S. Org. Coat. and Plast. Preprints, 4, 475 (1979).

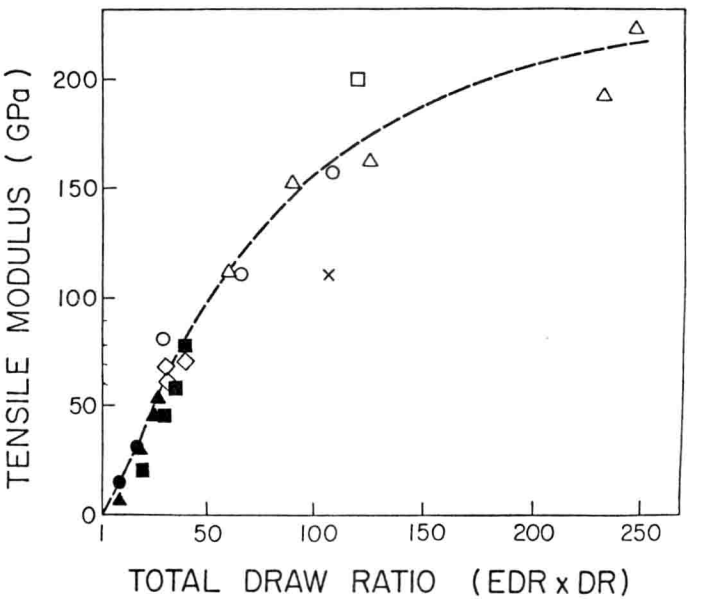

Figure 1: Solid State Extrusion Draw of Single Crystal Mats of UHMWPE to an Extrusion Draw Ratio (EDR) Followed by Conventional Draw (DR) at 110°C.