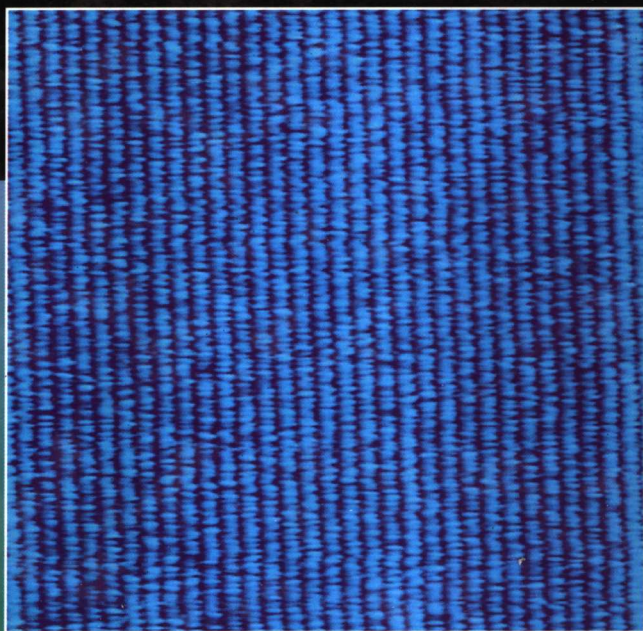


WILEY SERIES IN POLYMER SCIENCE



# MODERN FLUOROPOLYMERS

Atomic micrograph showing chains of Teflon®



HIGH PERFORMANCE  
POLYMERS FOR  
DIVERSE  
APPLICATIONS

Edited by **John Scheirs**

# Modern Fluoropolymers

High Performance Polymers for  
Diverse Applications

Edited by

**John Scheirs**

ExcelPlas Australia, Moorabbin, Victoria, Australia

WILEY SERIES IN POLYMER SCIENCE

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# Series Preface

The Wiley Series in Polymer Science aims to cover topics in polymer science where significant advances have been made over the past decade. Key features of the series will be developing areas and new frontiers in polymer science and technology. Emerging fields with strong growth potential for the twenty-first century such as nanotechnology, photopolymers, electro-optic polymers etc. will be covered. Additionally, those polymer classes in which important new members have appeared in recent years will be revisited to provide a comprehensive update.

Written by foremost experts in the field from industry and academia, these books place particular emphasis on structure-property relationships of polymers and manufacturing technologies as well as their practical and novel applications. The aim of each book in the series is to provide readers with an in-depth treatment of the state-of-the art in that field of polymer technology. Collectively, the series will provide a definitive library of the latest advances in the major polymer families as well as significant new fields of development in polymer science.

This approach will lead to a better understanding and improve the cross fertilisation of ideas between scientists and engineers of many disciplines. The series will be of interest to all polymer scientists and engineers, providing excellent up-to-date coverage of diverse topics in polymer science, and thus will serve as an invaluable ongoing reference collection for any technical library.

Dr John Scheirs  
Series Editor  
June 1997



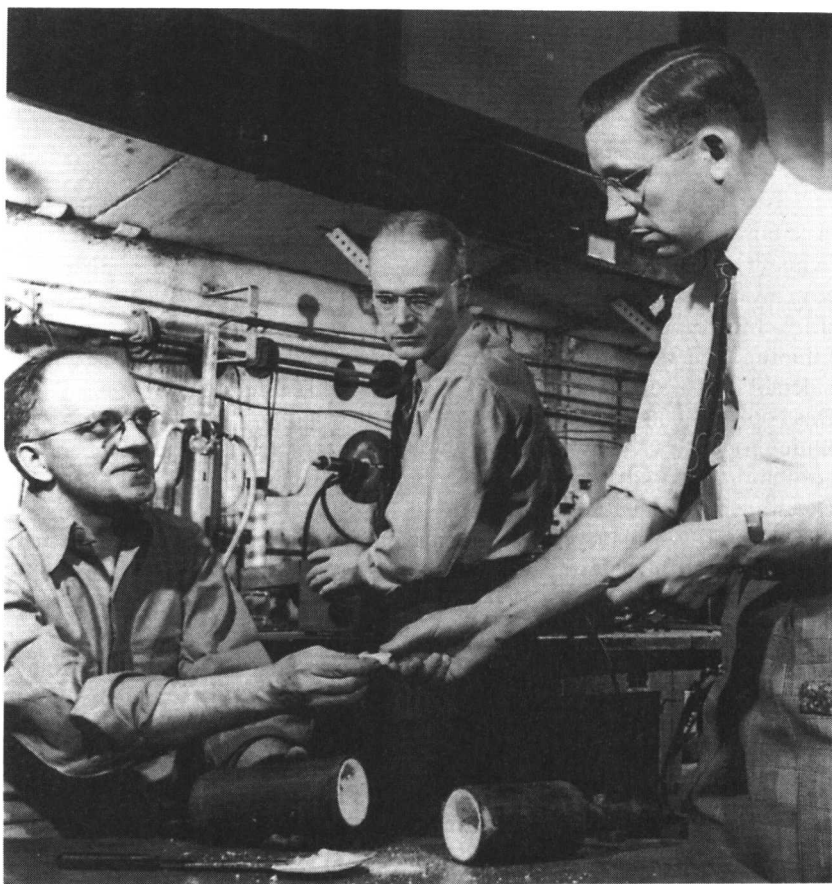
# Preface

The last book on fluoropolymers was published in 1972 (edited by Dr. Leo Wall) and while it was a comprehensive overview of fluoropolymer development at that time, many of the polymers described therein have failed to reach commercial maturity. Moreover, the last 25 years have seen the introduction of numerous new fluoropolymers and fluoroelastomers and these developments have widened considerably the scope and applications of fluorine-containing polymers.

This book presents an overview of modern fluoropolymers with an emphasis on structure/property behaviour and their diverse fields of application. The incorporation of fluorine into both organic and inorganic polymers confers hydrophobicity, enhanced thermal, chemical and oxidative stability, reduced adhesion, increased solubility, improved biocompatibility and increased gas permeability. The introduction of fluorine in the form of hexafluoroisopropylidene groups can also impart solubility and processability to otherwise largely intractable polymers such as polyimides and polybenzimidazoles (see Chapter 8).

From a historical perspective, fluoropolymer developments have always been closely linked to military and strategic applications. For example, PTFE from the Du Pont pilot plant which began in 1943 was utilized almost immediately at Oak Ridge, Tennessee, in equipment for separating the isotopes of uranium for the first atomic bomb. PTFE also found military use as a nose cone cover for artillery shells in World War II. Even before this, extensive work was done on a partially fluorinated polymer, PCTFE, in order for it to be used in the Manhattan atomic bomb project. In a series of parallel developments, PCTFE was independently developed in Germany by the chemical giant IG Farben. Then in the early 1940s, PVF came into commercial production in the US while pilot-plant production of PTFE was carried out in the UK at ICI in the period 1944–47.

In 1948, another polymer which began with a promising future was polyfluoroprene (the polymer of 2-fluoro-1,3-butadiene). It was officially the first commercial fluoroelastomer though it was surpassed by the development of Kel-F (VDF–CTFE) in 1954 by the US Army and Viton VDF–HFP-type fluoroelastomers in 1958 since these showed vastly superior properties. The emerging aerospace industry in the early 1950s spurred the development of these



Discovery of PTFE (Teflon®) inside a cylinder of tetrafluoroethylene (TFE) gas by Dr Roy Plunkett (right) in the DuPont Laboratories in 1938. (Courtesy of DuPont)

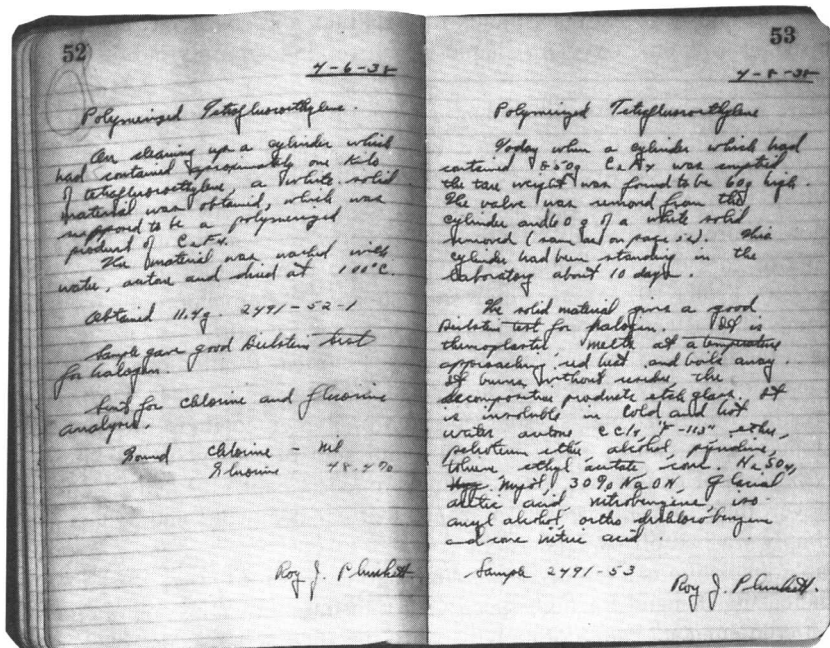
fluoroelastomers in response to the critical need for rubbers with better heat and fuel resistance to be used in seals and hoses for military jet engines.

Later other fluoroelastomers were developed by the US Air Force for seals on their experimental supersonic aircraft. While the use of fluoropolymers in military and strategic applications still continues to drive fluoropolymer research, see for example submarine radome coatings (Chapter 6), F-111 fuel tank seals (Chapter 20), lubrication seals for B-series strategic bombers (Chapter 19), perfluoropolyether liquids as lubricants for bearings in UF<sub>6</sub> enrichment plants as well as for satellites (Chapter 24), canopies for supersonic fighter aircraft (Chapter 9) and heat-resistant shields for satellites and spacecraft coatings that are resistant to atomic oxygen (Chapter 4), there are also a myriad of terrestrial applications.

Apart from high-tech military applications, fluoropolymers touch our daily lives in a number of diverse ways, from the breathable Gortex<sup>®</sup> material in sporting and outdoor wear based on fibrillar PTFE to Scotchgard<sup>®</sup> coatings (fluorinated acrylic esters polymers) which impart water and oil repellency. In addition, fluoroelastomer tubes and seals are now extensively used in the fuel systems of cars due to their excellent resistance to methanol and low permeation (see Chapter 19). Another diverse application area of fluoropolymers is as lubricants (liquid perfluoropolyethers) in computer hard-drives to prevent wear between the head and the spinning hard disk. Fluorinated polymer lubricants are even used to lubricate the delicate mechanisms of Rolex<sup>®</sup> watches. Furthermore, on prestige buildings and skyscrapers, fluoropolymer coatings provide excellent long-term durability since they show no sign of fading or cracking even after 25 years of continuous outdoor exposure (see Chapter 14 and Chapter 29). Moreover, their low surface energy means that streaks of dirt and adherent dust are simply washed off by rain.

Cable insulation is a rapidly expanding market area for fluoropolymers, given the increasing demand for high-speed data transmission cables for Internet and optical communications. Fluoropolymers are specified here because of their high temperature and fire resistance. The so-called 'plenum cables' that run in air-conditioning ducts and in the open spaces between ceilings and floors of offices are an application that can only be met by fluoropolymers by virtue of their low flame-spreading and low smoke-generating behaviour in a fire situation. Hook-up wires for trains and planes also represent another large application area for crosslinked fluoropolymers (see Chapter 18).

Amorphous perfluoropolymers are presently making major inroads as plastic optical fibres because of their high transparency in the near infra-red. In contrast, the presence of vibrational C-H overtone absorptions in the near infra-red spectrum of hydrocarbon polymers limits their use as optical fibres due to high signal losses by attenuation. Their low refractive index also makes fluoropolymers useful materials for fibre optic cladding applications. In addition, the hydrophobicity of fluoropolymers is advantageous for their use as optical fibres, since water



Laboratory notebook of Dr Roy Plunkett in which the discovery of Teflon® was first recorded on April 6, 1938. (Courtesy of DuPont)

absorption significantly increases losses in the near infra-red region used by the transmitting lasers.

Fluoropolymers are the only materials capable of withstanding the combination of high temperatures and high acidity encountered in flue gas desulphurizers in coal-burning power plants. Thus, in many cases, fluoropolymers perform in applications where no other materials can. In fact, lesser performing materials could prove hazardous or at the very least lead to increased maintenance and downtime if they were used in place of fluoropolymers (e.g. in the case of seals used in deep oil exploration).

Components such as O-rings, gaskets, seals, etc. usually represent the weak points in an engineering application and it is in these critical areas that fluoropolymers are frequently specified. Though fluoropolymers are used in very small volumes relative to commodity polymers their function is unique and instrumental to the overall performance of the application in which they are used. As a result, the chemical processing industry is heavily reliant on fluoropolymers and owes much of its development to their availability (see Chapters 16 and 25).

Fluoropolymer coatings, by virtue of their excellent UV resistance, have great potential to upgrade the service life of cheaper engineering plastics such as ABS (which on its own has very little resistance to weathering). This demonstrates the concept where the high-performance FP is used as a protective veneer on a cheaper substrate that provides mechanical integrity. This idea is also behind the wide use of fluoropolymer liners in steel pipes in chemical processing applications.

The excellent stability of fluoropolymers in the UV is becomingly increasingly important now that further miniaturization of electronic integrated circuitry is creating the need to reduce the wavelength of the light source used in resist manufacture from near- and mid-UV (300–450 nm) to far-UV (<250 nm). In particular, KrF excimer lasers (248 nm) are used currently for RAM fabrication and it is at such low wavelengths that most other polymers degrade.

Fluoropolymers are also characterized by their outstanding purity, and from this property numerous applications are derived. Their inertness combined with that fact they contain no additives, makes fluoropolymers the logical choice for high-purity pipes and fittings for the semiconductor and pharmaceutical industries.

Thus, from humble beginnings as a waxy deposit in a cylinder of refrigerant gas, certain grades of fluoropolymers now have the distinction of being the most expensive polymers commercially available (e.g. Teflon® AF) and combine the chemical inertness of PTFE with optical transparency and processability. The high cost of fluoropolymers is the result of complex manufacturing operations with multistep and exacting syntheses. For example, chapters on PFA (Chapter 11), Teflon® AF (Chapter 22) and Cytop® (Chapter 28) give an appreciation on the sequences of reactions involved. Even though the fluoropolymer product slate is now replete with a diverse range of commercially available fluoropolymers, new

ones continue to emerge. Examples of these include, MFA and THV, both of which were commercialized only in the past few years (see Chapters 21 and 13 respectively).

As with any family of polymers, fluoropolymers by and large share common strengths but also common deficiencies. However, within this large group of polymers, significant variability does exist in structure and properties. The challenge is no longer simply specifying a 'fluoropolymer for the job' over a non-fluorinated polymer, but rather to judiciously select the most suitable fluoropolymer grade. With this in mind the opening chapter is designed to convey an appreciation of the elements involved in selecting fluoropolymers and fluoroelastomers to avoid in-service failure and to enable more informed choices in material specification.

*John Scheirs*

# About the Editor

John Scheirs obtained a Ph. D. in Applied Science from the University of Melbourne, Australia. Subsequently, he worked as a development chemist in a development/technical service laboratory for the Exxon-Mobil polymer joint venture in Melbourne. In 1990, he spent one year as a guest researcher at Sussex University in the UK developing new, sensitive techniques for studying polymer degradation. From 1994 to 1996 he has been engaged in research in laboratories in Italy, Belgium and France. Dr Scheirs has authored over 50 scientific papers, including eight encyclopedia chapters and has given presentations at ACS, IUPAC and ANTEC symposia. He is on the editorial board of *Polymer Degradation and Stability*. Dr Scheirs is a member of the Society of Plastic Engineers (SPE), American Chemical Society (ACS), Institute of Materials (formally the PRI) and the Royal Australian Chemical Society (RACI). Current affiliation is with ExcelPlas Australia, a polymer consulting company. In the past two years he has worked on projects concerning the durability of fluoropolymers, particularly polyvinylidene fluoride and perfluoropolyethers.

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