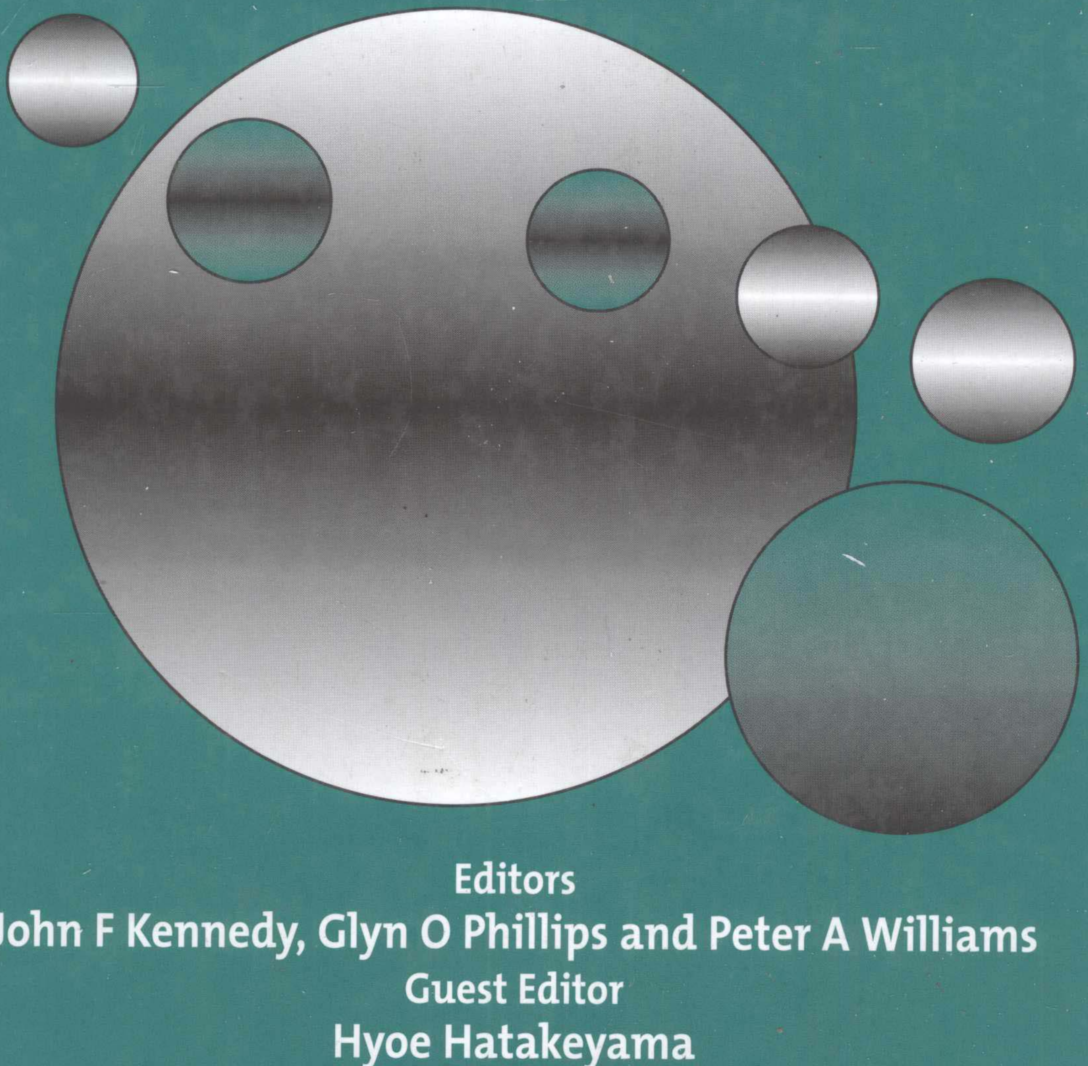
Recent Advances in Environmentally Compatible Polymers



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THE CELLUCON TRUST

Incorporating

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International Educational Scientific Meetings
on Cellulose, Cellulosics and Wood

Cellucon Conferences as an organisation was initiated in 1982, and Cellucon '84, which was the original conference, set out to establish the strength of British expertise in the international field of cellulose and its derivatives. This laid the foundation for subsequent conferences on carbohydrate etc. polymer topics in Wales (1986), Japan (1988), Wales (1989), Czechoslovakia (1990), USA (1991), Wales (1992), Sweden (1993), Wales (1994), Finland (1998), and Japan (1999). These conferences have had truly international audiences drawn from the major industries involved in the production and use of cellulose pulp and fibre derivatives of cellulose, plus representatives of academic institutions and government research centres. This diverse audience has allowed the cross-fertilisation of many ideas, which has done much to give the field of cellulose in its diverse forms the higher profile that it rightly deserves.

Cellucon Conferences are organised by The Cellucon Trust, an official UK charitable Trust with world-wide objectives in education in wood and cellulosics. The Cellucon Trust is continuing to extend the knowledge of all aspects of cellulose, lignin, hyaluronan and other national polymers world-wide. At least one book has been published from each Cellucon Conference as the proceedings thereof. This volume arises from the 1999 conference held in Tsukuba, Japan and the conferences planned to be held in the UK and in the USA etc, will generate further useful books in this area.

The 11th International
Cellucon Conference
CELLUCON '99

Recent Advances in Environmentally Compatible Polymers

ACKNOWLEDGEMENTS

This book arises from the International Conference – CELLUCON '99 – which was held at the Tsukuba Center for Institutes, Tsukuba. This Meeting owes its success to the invaluable work of its Organising Committees and its generous sponsors.

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PREFACE

Biopolymers such as polysaccharides, lignin, proteins and polyesters are a natural resource, being produced by living organisms. However, these compounds are not always useful for mankind. In order to compensate for the apparent unsuitability and inconvenience of natural polymers, various kinds of synthetic polymers have been developed by using petroleum and coal as raw materials. Recently, however, it has been found that most synthetic polymers are not compatible with the environment, since they cannot be included in the natural recycling system. They have therefore become less popular.

Mankind is presented with serious contradictions between the convenience of human life and compatibility with natural circumstances. It is easy to say that we have to return to nature in order to solve the problems of man-made material. However, this means that we lose all the convenient features and materials which science has developed throughout human history. Accordingly, we have to accomplish a form of 'sustainable development', maintaining our present life, developed by science, along with compatibility.

In the polymer industry, utilization of plant and animal components is the key to sustainable development. Carbohydrates have already been used significantly in the food, medical and cosmetic industries. Plant materials such as cellulose, hemicellulose and lignin are the largest organic resources but with the exception of cellulose, they are not very well utilized. Hemicellulose is significantly under-utilized. Lignin, production of which is over twenty million tons per year worldwide, is mostly burnt as fuel and only increases the amount of carbon dioxide in the environment, although lignin is one of the most useful natural resources.

We have to understand that nature constructs a variety of materials that can be used for human life. Physical properties of biomaterials cover the range from viscous liquids to solids. The complexity of biomaterials is based on the intricacies of their complex molecular architectures. However, scientific advances enable us to understand molecular features of biomaterials through modern analytical methods such as infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermal and mechanical analysis and electron microscopy. Now is the time to consider that the compounds produced through biosynthesis can be used as "ready-made" raw materials for the synthesis of useful plastics and materials for human life. Is it possible for example, to convert plant components to high-performance and highly functional materials? Of course, the answer is 'Yes'. Major plant components, such as carbohydrates and lignin, contain highly reactive hydroxyl groups that can be used as reactive chemical reaction sites. Using the reaction sites, it is possible to convert carbohydrates and lignin, for example to gels, membranes, functional polymers, engineering plastics and biodegradable polymers that are environmentally compatible.

This book, which is the proceedings of the International Cellucon Conference 99 (Japan) is divided into several sections. It commences with the keynote lecture which offers an overview of basic reactions which occur in the degradation of important polymers. The section on Synthesis and derivatisation of biocompatible polymers includes various reaction routes for the production of useful polymers and their derivatives from plant components. The section on production and use of biocompatible materials offers a material design lesson on the architectural methods to relate chemical structures of biocompatible polymers to their physical properties. The section on biodegradable polyurethane-based polymers reports the recent development in preparation and physical properties of polyurethanes from biomass. The section on analysis and characterisation of new polymers and materials covers the application of CPMAS NMR, X-ray analysis, differential scanning calorimetry (DSC), thermogravimetry (TG), TG-Fourier transform infrared spectrometry conversion, modification and characterisation of biopolymers.

Collectively, the 56 papers cited in this book provide a perspective on the current state of knowledge of biomaterials science as it affects the structural, synthetic and biotechnological fields of environmentally compatible materials.

Hyoe Hatakeyama

Chairman
International Organising Committee for Cellucon '99

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PART 6: BIOENGINEERING OF NEW MATERIALS

Part 1

An overview of the degradation of polymer materials

DEGRADATION OF IMPORTANT POLYMER MATERIALS - AN OVERVIEW OF BASIC REACTIONS

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1. Introduction

The main theme of this conference is related to environmentally compatible polymers. Because most commercial polymer materials are of high molecular mass they have as such insignificant biological effects. Their degradation products and the additives of low molecular mass may, however, affect the environment. Therefore, it is essential to know the basic reactions of degradation for the important polymer materials used in large amounts.

Environmental effects of polymer materials are decreased when the materials are reused (recirculated) in some way. To maintain useful properties of the materials degradation should be under control and brought to a minimum, i.e. stability retained. Also during recirculation, it is important to know what basic degradation reactions may occur and affect the properties.

2. Degradation Reactions

2.1. Degradation reactions of polymer materials are initiated in various ways related to the conditions to which the materials are exposed. A common first degradation step is radical formation by main valence bond scission which may be caused by high energy radiation, absorption of ultraviolet or even visible light, mechanical stress or a high velocity gradient, molecular motion at high temperature or electron injection at high voltage. The polymer radicals formed react easily with molecular oxygen in triplet (biradical) state which is the ground state for atmospheric oxygen.

2.2 Polymers containing double bonds or conjugated double bonds react easily by addition of molecular oxygen in excited singlet state and with ozone (O_3) which decomposes to singlet oxygen and atomic oxygen. This is the "ene" reaction with singlet oxygen which causes oxidation and bond scission. Atomic oxygen may abstract hydrogen from the polymer which gives radical formation.

2.3. Polymers containing ester, amide and ether bonds in their main chain degrade by hydrolysis. This is an ionic reaction which is catalyzed by acid and alkali in the presence of water and is faster at elevated temperature.

2.4 Many polymer materials are degraded in biologically active media and the enzymes involved may have various initiation functions, e.g. catalyze hydrolysis, cause oxidation of C-H groups to C-OH, give proton transfer, etc.

The four types of basic degradation reactions will be further described and exemplified for the important commercial polymer materials.