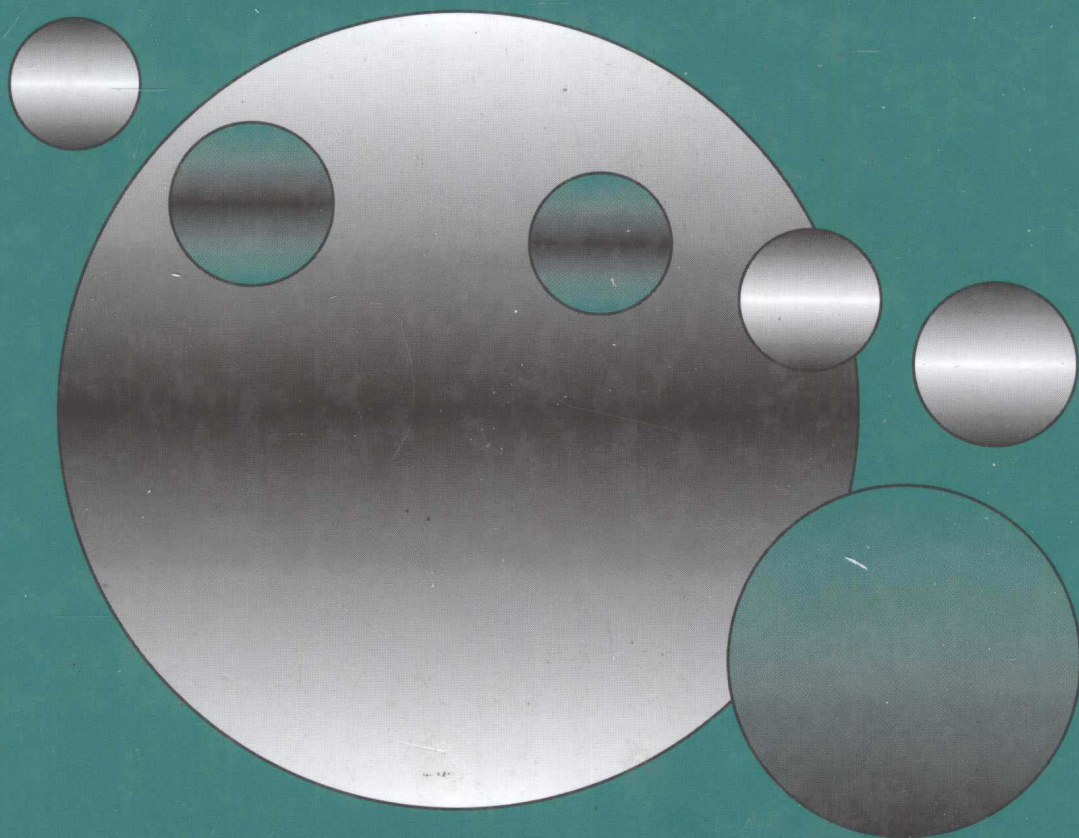


Recent Advances in Environmentally Compatible Polymers



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RECENT ADVANCES IN ENVIRONMENTALLY COMPATIBLE POLYMERS

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THE CELLUCON TRUST

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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 natural 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.

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**The 11th International
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Recent Advances in Environmentally Compatible Polymers

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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.

Hyoë Hatakeyama

*Chairman
International Organising Committee for Cellucon '99*

CONTENTS

Preface	xv
PART 1: AN OVERVIEW OF THE DEGRADATION OF POLYMER MATERIALS	
1. Degradation of important polymer materials – an overview of basic reactions B Rånby	3
PART 2: SYNTHESIS AND DERIVATISATION OF BIOCOMPATIBLE POLYMERS	
2. Conjugated oligomers bearing furan and thiophene heterocycles: synthesis, characterization and properties related to electronic conduction and luminescence C Coutterez and A Gandini	17
3. Polyamides incorporating furan moieties. Novel structures and synthetic procedures M Abid, S Gharbi, R El Gharbi and A Gandini	27
4. Saccharide- and lignin-based polycaprolactones and polyurethanes H Hatakeyama, Y Izuta, T Yoshida, S Hirose and T Hatakeyama	33
5. Cellulose as a raw material for levoglucosenone production by catalytic pyrolysis G Dobeles, G Rossinskaja, T Dizhbite, G Telysheva, S Radtke, D Meier and O Faix	47
6. New ionic polymers by subsequent functionalization of cellulose derivatives M Vieira, T Liebert and Th Heinze	53
7. Preparation and characterization of carbamoyl-ethylated and carboxyethylated konjac mannan S Takigami, Y Suzuki, A Igarashi and K Miyashita	61
8. Plastification of cellulosic wastes M Durán, M Moya, E Umaña and G Jiménez	67
9. Synthesis and thermal properties of epoxy resins derived from lignin S Hirose, M Kobayashi, H Kimura and H Hatakeyama	73
10. Effect of modification on the functional properties of rice starch M A M Noor and M N Islam	79

11. **Succinylation of chemically modified wool keratin – the effect on hygroscopicity and water absorption**
N Kohara, M Kanei and T Nakajima 91
12. **Natural polymers for healing wounds**
J F Kennedy, C J Knill and M Thorley 97

PART 3: PRODUCTION AND USE OF BIOCOMPATIBLE MATERIALS

13. **Improvement of alginate fiber mixing with phosphoryl polysaccharides**
S Tokura, H Tamura, Y Tsuruta, C Nagaei and K Itoyama 107
14. **Preparation of cellulose viscose for various matrices**
B Lönnberg, S Ciovica, T Strandberg, T Hultholm and K Lönnqvist 113
15. **Synthesis and properties of novel polyelectrolyte on the basis of wood polymer**
G Shulga, G Zakis, B Neiberte and J Gravitis 123
16. **Utilising the potential of wood fibre**
L Salmén and U-B Mohlin 129
17. **Composites from banana tree rachis fibers (*Musa Giant Cavendishii* AAA)**
M Sibaja, P Alvarado, R Pereira and M Moya 139
18. **Temperature and concentration dependency on equilibration in polysaccharide electrolyte hydrosol**
M Takahashi, M Mishima, T Yamanaka, T Hatakeyama and H Hatakeyama 145
19. **Hydrolysed lignin. Structure and perspectives of transformation into low molecular products**
M Ja Zarubin, S R Alekseev and S M Krutov 155
20. **Products of lignin modification: promising adsorbents of toxic substances**
T Dizhbite, A Kizima, G Rossinskaya, V Jurkane and G Telysheva 161
21. **Characterisation and adsorption of lignosulphonates and their hydrophobized derivatives on cellulose fibre and inorganic fillers**
G Telysheva, T Dizhbite, A Kizima, A Volperts and E Lazareva 167

PART 4: BIODEGRADABLE POLYURETHANE-BASED POLYMERS

22. **Biodegradable and highly resilient polyurethane foams from bark and starch**
J-J Ge, W Zhong, Z-R Guo, W-J Li and K Sakai 175

23. Biodegradable polyurethanes derived from waste in the production of bean curd and beer K Nakamura, M Iijima, E Kinoshita and H Hatakeyama.....	181
24. Biodegradable polyurethane composites containing coffee bean parchments H Hatakeyama, D Kamakura, H Kasahara, S Hirose and T Hatakeyama	191
25. Biodegradable polyurethane sheet derived from waste cooking oil S Srikumlaithong, C Kuwarananchaoen and N Asa	197
26. Biodegradable polyesters prepared with dimethyl succinate, butanediol and monoglyceride Y Taguchi, A Oishi, K Fujita, Y Ikeda and T Masuda	205
27. Preparation and thermal properties of polyurethane composites containing fertilizer N Yamauchi, S Hirose and H Hatakeyama.....	211
28. Biodegradable polymers derived from lactide and lactic acid S H Kim and Y H Kim.....	217
29. Biodegradable polyurethane foams from molasses Y Hazutani	227
30. Biodegradable polyurethane foams derived from molasses K Kobashigawa, T Tokashiki, H Naka, S Hirose and H Hatakeyama.....	229
31. Polyurethane from pineapple wastes M Moya, J Vega, M Sibaja and M Durán	235
32. Preparation and physical properties of saccharide-based polyurethane foams Y Asano, H Hatakeyama, S Hirose and T Hatakeyama.....	241
33. Biodegradable polymer in seed protein from corn J Magoshi and S Nakamura.....	247

PART 5: ANALYSIS AND CHARACTERISATION OF NEW POLYMERS AND MATERIALS

34. The complete assignment of the ^{13}C CP/MAS NMR spectra of native cellulose by using ^{13}C labelled glucose T Erata, T Shikano, M Fujiwara, S Yunoki and M Takai	261
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35. ^{13}C CP/MAS NMR and X-ray studies of cellooligosaccharide acetates as a model for cellulose triacetate H Kono, Y Numata, N Nagai, M Fujiwara, T Erata and M Takai	269
36. Thermal and mechanical properties of cellulose acetates with various degrees of acetylation in dry and wet states T Asai, H Taniguchi, E Kinoshita and K Nakamura.....	275
37. DSC and TG studies on cellulose-based polycaprolactones H Hatakeyama, H Katsurada, N Takahashi, S Hirose and T Hatakeyama	281
38. TG-FTIR studies on cellulose acetate-based polycaprolactones T Yoshida, H Hatakeyama, S Hirose and T Hatakeyama	289
39. Thermal analysis of functional paper by a temperature modulated technique T Hashimoto, W-D Jung and J Morikawa	295
40. DSC studies on the structural change of water restrained by pectins M Iijima, K Nakamura, T Hatakeyama and H Hatakeyama	303
41. Thermal properties of wood ceramics by TG-MS and CRTG T Arii and M Momota	311
42. Application of environment controlled thermomechanical analysis system H Katoh, T Nakamura and N Okubo	317
43. Effect of water on molecular motion of alginic acid having various guluronic and mannuronic acid contents M Takahashi, Y Kawasaki, T Hatakeyama and H Hatakeyama	321
44. Effect of the initial state on the sorption isotherm and sorption kinetics of water by cellulose acetate H Gocho, A Tanioka and T Nakajima	327
45. Osmometric and viscometric studies on the coil-helix transition of gellan gum in aqueous solutions E Ogawa	333
46. Weathering analysis of modified poly (2,6-Dimethyl-1,4-Phenylene ether) by thermal analysis Y Nishimoto, K Sato, Y Nagai and F Ohishi	341
47. Non-desirable carbohydrate reactions in pulping and bleaching G Gellerstedt and J Li	347

PART 6: BIOENGINEERING OF NEW MATERIALS

48. Precision analysis of biosynthetic pathways of bacterial cellulose by ^{13}C NMR	
M Fujiwara, Y Osada, S Yunoki, H Kono, T Erata and M Takai	359
49. Studies of transglycosylation of cellobiose by partially purified <i>trichoderma viride</i> β-Glucosidase	
H Kono, M R Waelchli, M Fujiwara, T Erata and M Takai	365
50. Celsol – modification of pine sulphate paper grade pulp with <i>Trichoderma Reesei</i> cellulases for fibre spinning	
P Nousiainen and M Vehviläinen	371
51. Formation and characterization of transformed woody plants inhibiting lignin biosynthesis	
N Morohoshi and Y Tsuji	379
52. Characterization and utilization of ligninolytic enzymes produced by basidiomycetes	
M Kuwahara	387
53. Kinetics of biodegradation of <i>n</i>-alkanes by <i>pseudomonas</i> immobilised in reticulated polyurethane foam	
M G Roig, J F Kennedy, C J Knill, J M Sanchez, M A Pedraz, H Jerabkova and B Kralova	397
54. Biocompatible aspects of poly (2-methoxyethylacrylate) (PMEA) – the relationship between amount of adsorbed protein, its conformational change, and platelet adhesion on PMEA surface	
M Tanaka, T Motomura, M Kawada, T Anzai, Y Kasori, T Shiroya, K Shimura, M Onishi, A Mochizuki and Y Okahata	405
55. Isolation of a lignin-degrading laccase and development of tranformation system in <i>Coriolus Versicolor</i>	
Y Nitta, Y Iimura, J Mikuni, A Fujimoto and N Morohoshi	411
56. Effect of biodegradable plastics on the growth of <i>Escherichia coli</i>	
A Nakayama, N Yamano, S Fujishima, N Kawasaki, N Yamamoto, Y Maeda and S Aiba	419
Index	425

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.