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Organizer



International Centre  
for Science and High Technology

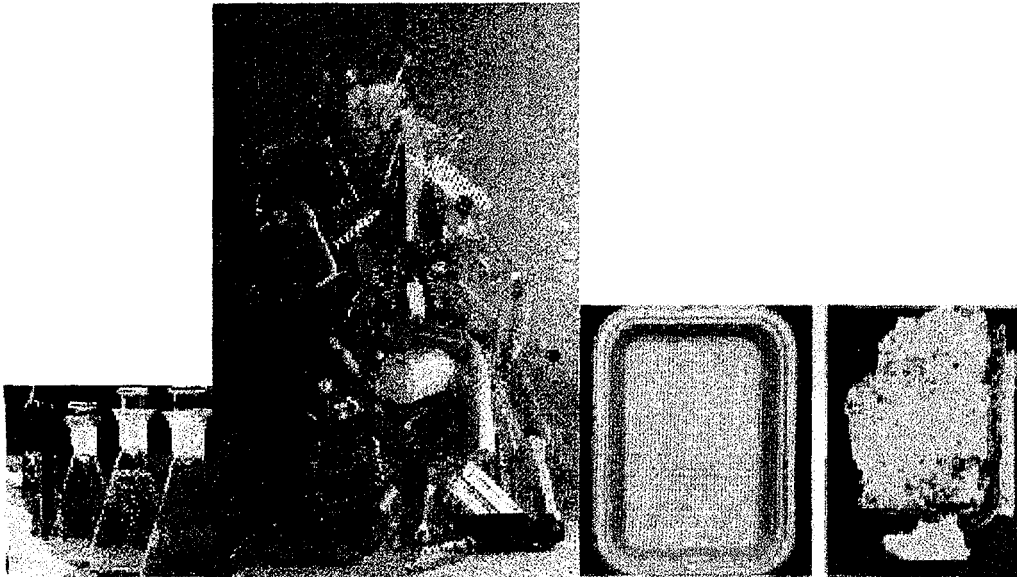
Trieste, Italy

ICS-UNIDO Workshop on

***Environmentally Degradable Polymers:***

***Environmental and Biomedical Aspects***

***September 12-19, Antalya, Turkey***



# ***FINAL REPORT***

UNIDO Project: TF/GLO/96/105

Contract No: 98/198

Local Organizer:



Hacettepe University, Ankara, Turkey

6

# CONTENT

	<u>Page No</u>
<b>1. SUBJECT ---- OBJECTIVES</b>	<b>2</b>
<b>2. ORGANISATION</b>	<b>3</b>
Organizators	3
Site	3
Founding	4
Lectures and Presentation	4
Participants --- Financial support towards their expenses	5
Social Events	5
<b>3. ASSESMENTS ---- CONCLUSIONS</b>	<b>6</b>
<b>4. APENDIXES</b>	
Appendix I: Financial Report	
Appendix II: Programme	
Appendix III: Abstracts	
Appendix IV: Lecture/Presentation Notes	
Appendix V: Participant List	

## 1. SUBJECT ---- OBJECTIVES

Today, polymers are used in the production of a wide variety of materials for diverse applications. The expectations in the 21st century for polymeric materials demand are in favor of a 2 to 3 fold increase of polymeric materials production as a consequence of the increase in their consumption especially in the developing countries. In the next couple of decades the overall production of polymeric materials is expected to reach a value as high as 350-400 million tons per year. Therefore a one order of magnitude jump in the polymer consumption, with respect to the present annual level can be envisaged for those countries with a per capita share lower than 5-10 kg, once the living standards of the developed countries is reached.

The high production and consumption of polymeric materials have already brought in sight the environmental aspects of polymeric waste which has promoted all over the World a great deal of actions aiming to provide adequate solutions for minimizing this negative impact. There are constrains and regulations already operative or to be issued in the near future dealing with this subject. Burial in landfill sites, incineration with energy recovery, and mechanical or chemical recycling are presently adopted alternative technologies available for the management of polymeric waste. Use of biodegradable polymers which may replace the conventional commodity polymers in those segments in which other waste management approaches are difficult to utilize and/or uneconomical, have been considered as one of the novel alternative approaches. In this approach it is expected that the materials made of biodegradable polymers stay stable during processing, storage and use, but do undergo degradation under environmental conditions in the waste. **One of two main objectives of this ICS-UNIDO workshop was to evaluate trends in "biodegradable polymers" used mainly in commodity polymeric materials by focusing on "environmental aspects".**

Polymers have also being utilized very widely as biomaterials in medicine to replace a diseased or damaged part of the body, to assist in healing, to improve function, to correct cosmetic problems, to aid treatment, and for diagnosis. In these applications, polymers do come into contact with the soft and/or hard tissues or the cardiovascular blood system, or with both. Non-biocompatible materials may be rejected and also may cause important side effects. Therefore, in addition of the required properties depending on their final use, polymeric materials must meet certain criteria and regulatory requirements before they can be qualified for use in biomedical applications. Both nondegradable and biodegradable polymers are used as biomaterials in different forms. Biomaterials made of biodegradable polymers, mainly temporary artificial implants, are designed to degrade in vivo in a controlled manner over a predetermined period, which eliminates a secondary surgery to remove the material after serving their intended purpose. **The second main objective of the this workshop was to evaluate present and future trends in "biodegradable polymers" used in more specialty polymeric materials, namely in biomaterials by focusing on "biomedical aspects".**

Moreover, country reports and case studies should indicate the state-of-the art in the relevant developing and transition countries.

## 2. ORGANISATION

### *Organizators*

The Workshop was jointly organized by the International Centre for Science and High Technology (ICS) and Hacettepe University which was the contractor (as recognized by UNIDO) and local organizer. Hacettepe University is among the leading universities in Turkey with about 20000 students and over 1000 faculty, and is given credit with its unique structure and relations with the industry related to environmental, polymer, medical technologies which are directly related to the subject of the workshop Workshop. The local organization committee consisted of the following members who were also actively attended the Workshop:

Prof. Dr. Süleyman Sağlam (Honorary President of the Workshop, Rector of Hacettepe University)  
 Prof. Dr. Erhan Pişkin (Chairman of the Workshop, Hacettepe University, Chemical Eng. Dept.)  
 Dr. Ahmet Kozluca (Hacettepe University, Chemical Eng. Dept.)  
 Güldem Güven (Hacettepe University, Chemical Eng. Dept.)  
 Hülya Yavuz (Hacettepe University, Environmental Eng. Dept.)  
 Kemal Kesenci (Hacettepe University, Bioengineering Dept.)  
 Volga Bulmuş (Hacettepe University, Bioengineering Dept.)

The international scientific committee was formed from the following members who advised local organization committee on the content of the scientific programme and also actively participated the workshop by delivering lectures.

Prof. Dr. Stanislav Miertus (ICS, Trieste, Italy)  
 Prof. Dr. Emo Chiellini (Pisa University, Pisa, Italy)  
 Prof. Dr. Erhan Pişkin (Hacettepe University, Ankara, Turkey)

### *Site*

Turkey was selected as the site of the Workshop by considering the following points: Turkey is a both geographically and socially a bridge in between Europe and Asia. It has borders (or surrounded by) with several European (Greece, Bulgaria, Romania, Russia, etc.) and Middle East (Iran, Iraq, Syria) countries. It has tight connections with ex-Soviet Union Countries (Azerbaijan, Kazakhstan, Turkmenistan, Armenia, etc.). Moreover, Turkey is a fast developing country with a high interest in polymer production and processing. Therefore, the meeting site was considered as a very suitable place to transfer the know-how and technology from developed countries to developing countries (or countries in transition) both at the R&D and industrial production levels.

Antalya Dedeman Hotel has been selected due to its conference facilities. This hotel is known as one of the first choices for scientific events. Almost all participants of the Workshop found the meeting place excellent by considering the quality of facilities and services and also rooms, food and social activities.

## *Founding*

The Workshop was mainly sponsored by ICS-UNIDO through the UNIDO Project (TF/GLO/96/105, Contract No: 98/198, the amount is 43650 US Dollars) given to Hacettepe University. The hosting institution, Hacettepe University covered the expenses related to secretariat, communications, mail services and using other facilities for the organization until the Workshop, which was estimated as roughly equal to an amount of 8000 US Dollars. Some of the participants (mainly from Hacettepe University) were supported from an Hacettepe University project supported by NATO Science for Stability Programme entitled "TU-BIOMAT" which is directed by Prof. E. Pişkin, through the budget saved for training (the amount is about 6000 US Dollars).

## *Lectures and Presentations*

The Workshop was officially opened with two welcome addresses delivered by Prof. S. Sağlam (Rector, Hacettepe University) and Prof. S. Miertus (ICS, Trieste, UNIDO). There were about 39 oral presentations (lectures and presentations as Country Reports) as given in the Programme (see the Programme in Appendix II). Unfortunately three of them were not presented because the presenters were not able to attend the Workshop because of the last moments problems/changes. There were also 5 poster presentations which were hanged out in a special room during the Workshop. The abstracts of the lectures/presentations which were arrived before 12<sup>th</sup> of September 1998 are given in Appendix III. EUROKA was represented by the EUROKA Chairmanship Office at TİDEB-TÜBİTAK located in Ankara and they had an exhibition during the Workshop at the same room with the posters. The lectures/presentations were delivered in the sessions realized from 9.00-13.30 and 17.30-19.30 every day. The time between 13.30-17.30 were used for lunch and the spare time to allow the participants to get together unofficially in a relaxing atmosphere to exchange the existing knowledge and to discuss issues on environmental and biomedical aspects in small groups.

The following points were presented and discussed in the lectures/presentations (see lecture notes in Appendix IV) presented by both international and national lecturers/speakers (see the list of participants in Appendix V).

- Biodegradation: definitions and basic principles
- Overview of environmentally degradable polymers
- Present status of environmentally polymers in commodity materials in use: types, synthesis, processing, applications, and **environmental aspects**
- Present status of environmentally polymers in biomaterials: types, synthesis, processing, applications, and **biomedical aspects**
- General discussions: use of environmentally polymers/materials in different countries, limitations/regulations, future perspectives.

Note that the copies of both the abstracts and lecture/presentation notes were provided to the participants during the Workshop. A copy of these documents were also included along with this final report. The full written papers were collected from the presenters. Some of them were kind enough to bring the copies with them (which were also delivered to the participants during the Workshop), the others are willing to send the manuscripts later. The deadline is 30 October 1998. The manuscripts which will be collected by that time will be sent to ICS-UNIDO, Trieste, Italy for possible publication of a Proceedings.

### ***Participants --- Financial support towards their expenses***

The participants list is given in Appendix IV, which was prepared just before the Workshop started. Unfortunately, some of the participants (especially from abroad) did not appear at the meeting even though they had been confirmed their participation by that time.

The number of International Lecturers was ten as originally proposed in the "Terms of References". Note that Prof. S. Miertus from ICS was also included in this list. The lecturers were almost fully supported (towards to both travel and accommodation expenses) by the UNIDO project budget. Except, Prof. S. Miertus was covered his own expenses by ICS-UNIDO. Almost half of the international lecturers were from industry as required by UNIDO.

Total 17 international participants were selected to the Workshop (see Appendix V). About 40% of these participants were from industry or related institutions. We were planning to cover accommodations of 15 of them and give travel grants to 8 of them, as proposed in "Terms of References". M. Albosifi (from Libya), E. Cojocaru (from Romania), Prof. S. Kandil (from Egypt) and Dr. B.Z. Tang (from Hong Kong) were confirmed their attendance but not participated. We covered accommodations of 12 international participants, and give travel support to 9 of them.

There were three national lecturers/speakers which includes Prof. S. Sağlam, the rector of Hacettepe University (the honorary president of the Workshop) who delivered the opening speech. We also covered the travel and accommodation expenses of Prof. Sağlam in addition two other national lecturers.

The list of national participants is also given in Appendix V. 23 participants were selected from Turkey. 80% of this number was from industry or private institutions. The accommodation of 14 (among 23 national participants) were covered by the UNIDO project budget, other were self-supporting or covered from other sources.

### ***Social Events***

Special tables were reserved for the lunches and dinners at the restaurant which allowed the participants to meet informally. The Turkish Night including special food and show which was organized by the Hotel gave a chance to the participants to have a taste about Turkish Culture. An excursion was realized on 15<sup>th</sup> of September (Wednesday) which was a good opportunity for the participants to visit the surroundings of Antalya.

### 3. ASSESMENT — CONCLUSIONS

The Workshop was assessed by the participants via optional questionnaires. Participants evaluated the organization as being very good to excellent from both scientific and social point of view. Most respondents felt that the duration of the Workshop was "just right". Both the lectures and country reports were found very good and informative. There is now a greater awareness regarding environmentally degradable polymers and the importance of their environmental and biomedical use. Participants believe that the knowledge transferred and contacts that have been realized during the Workshop would certainly trigger the research and development programmes and activities in their countries, and they have already showed their interest in taking a part in future cooperative institutions/programmes in ICS Network. Several proposals of industries (from Turkey and Kuwait) have been presented to explore, through ICS, the possibility of implementation of EDP production in these countries. The main shortage (or limitation) of the organization which was pointed out by participants and also was faced by the local organizer was the timing of the announcement (invitation). This was of course due to late approval of the budget for the organization (which was at the end of July 1998).

The following points can be stressed as a more general conclusion of the Workshop. As we are approaching a new millennium, there are drastic changes all over the World in regards to environmental issues. The "Only One Earth" concept has now been widely accepted understanding that the humanity shares common environmental values and posterity will share a common future; in this sense, interactions between development and the environment must be taken into consideration in all aspects at the national, regional and global levels. The attainment of sustainable development on a global scale depends, on the first place, upon the attainment of a certain level of development by the countries in transition. In this connection the basis of an international economy policy should be provision of technical and financial support to contribute to the development of these countries. It is obvious that the countries in transition where the environmental problems have often emerged more recently than in the developed countries, have yet to learn the most effective use of the resources for environmental purposes, as compared to the developed countries who accumulated some experience in coping with these problems. The transmission of the experience in the developed countries to the countries in transition will allow them to take actions more swiftly, without wasting human and financial resources and without repeating the mistakes done by the developed countries. The high production and consumption of polymeric materials have brought in sight the environmental aspects of polymeric waste which has promoted all over the World a great deal of actions aiming to provide adequate solutions to minimize this negative impact. Use of environmentally degradable in specific applications would certainly be one of the most important alternative solutions. **Finally, the efforts of the ICS-UNIDO on this respect by organizing activities like this workshop, together with the promotion of common projects, would certainly add important pieces to this very complex puzzle to come up with concrete solutions to prevent further pollution of our beautiful planet.**



# TRAVEL EXPENSES

The names of the participants who received supports towards their travel expenses and the amounts paid are given below, and the copies of the related documents are attached.

## International Lecturers

1. Prof. E. Chiellini, Pia, Italy	700 USD
2. Prof. M. Çakmak, Akron, USA	700 USD
3. Dr. B. E.M. Lemmes, Anwerb, Belgium	600 USD
4. Prof. C. Migliaresi, Trento, Italy	410 USD
5. Prof. R. Narayan, Michigan, USA	700 USD
6. Prof. R. Ottenbrite, Richmond, USA	700 USD
7. Dr. R. L.Reis, Porto, Portugal	600 USD
8. Prof. G. Scott, Richmond, UK	994 USD

## International Participants

1. Prof. K. Djurabay	760 USD
2. Prof. A.A. Efendiev, Sumgait, Azerbaijan	600 USD
3. G. Köktürk, Akron, USA	700 USD
4. Dr. I. Lacik, Bratislava, Slovakia	400 USD
5. Prof. M Mebrahzadeh, Tehran, Iran	610 USD
6. Dr. A. Motta, Milano, Italy	400 USD
7. Prof. M. Rutkowska, Gdynia, Poland	400 USD
8. Dr. A.J. Varma, Pune, India	900 USD
9. Dr. S.R. Yang, Taipe, Taiwan	700 USD

## National Lecturers:

1. Prof. B. Hazer, Zonguldak, Turkey	215 USD
2. Prof. E. Pişkin, Ankara, Turkey	159 USD

**TOTAL: 11248 USD**

As described in the budget (see "Terms of References"), we have planned to cover travel expenses of 10 international lecturers + 8 international participants and 2 national lecturers. The total budget saved for this section was **12900 US Dollars**. As indicated above we supported 8 international lecturers + 9 international participants and 2 national lecturers. Still we have 1652 USD left in this budget. Therefore we covered accommodation of one more national participant by transferring 750 USD from here to the section itemized under the name of "Accommodation expenses" which is less than 10% (which is allowed).

# ACCOMODATION EXPENSES

As stated before the number of International Lecturers was 10 as originally proposed in the "Terms of References". Note that Prof. S. Miertus from ICS was also included in this list. Accommodation of these **9 international lecturers** were covered by the UNIDO project budget. Except, Prof. S. Miertus was covered his own expenses by ICS-UNIDO.

Total 17 international participants were selected to the Workshop (see Appendix V). We were planning to cover accommodations of 15 of them and give travel grants to 8 of them, as proposed in "Terms of References". M. Albosifi (from Libya), E. Cojocar (from Romania), Prof. S. Kandil (from Egypt) and Dr. B.Z. Tang (from Hong Kong) were confirmed their attendance but not participated. We covered accommodations of **12 international participants**.

There were 3 national lecturers/speakers which includes Prof. S. Sağlam, the rector of Hacettepe University (the honorary president of the Workshop) who delivered the opening speech. We also covered the accommodation expenses of these **3 national lecturers**.

The list of national participants is also given in Appendix V. 23 participants were selected from Turkey. The accommodation of **14 national participants** (among 23) were covered by the UNIDO project budget, other were self-supporting or supported by other sources (NATO Sfs Project).

Therefore, accommodations of a total of **38 participants** were covered from UNIDO budget (total amount 28500 US Dollars). Note that 750 US Dollars was transferred from the budget proposed for travel expenses (see the previous page). It was not possible to buy the accommodation of about 40 participants (about total 30 rooms) directly from hotels (because September is the highest tourist season in Turkey, and there was not enough time (the UNIDO project budget was approved at the end of July 1998) to make a prepayment for advanced reservation. Therefore the rooms were bought at Antalya Dedeman Hotel from N&M tourism who has a contingent. A special package fee was offered which was 750 USD for 8 days 7 nights per person (Sept. 12-19, 1998). This package fee includes stay, three meals including drinks, coffee breaks, conference facilities, etc. as also **indicated on the invoice**.

# TRANSPORTATION EXPENSES

As indicated in the “Terms of References” we have proposed a transportation expenses in our budget. N&M Tourism supplied also this service. The total is **3000 USD** as indicated on the enclosed invoice. This includes the transfer of the national participants from Ankara-Antalya-Ankara, daily transfer service during the Workshop in Antalya, and also transfer of the participants from and to Antalya Airport.

Organizer



International Centre  
for Science and High Technology

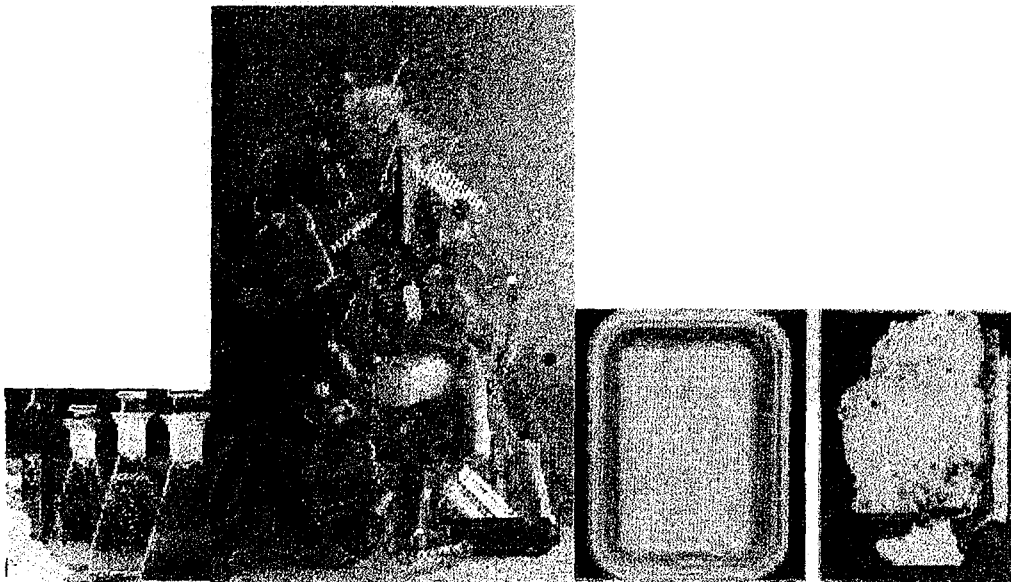
Trieste, Italy

ICS-UNIDO Workshop on

*Environmentally Degradable Polymers:*

*Environmental and Biomedical Aspects*

*September 12-19, Antalya, Turkey*



# *PROGRAMME*

Local Organizer:



Hacettepe University, Ankara, Turkey

***September 12, 1998, Saturday***

12.00 Arrivals

***September 13, 1998, Sunday***

- 9.00-9.50 **Welcome Speeches**  
*S. Sağlam*, President, Hacettepe University, Ankara, Turkey  
*S. Miertus*, ICS-UNIDO, Trieste, Italy
- 9.50-10.40 **Environmentally Degradable Polymers and Plastics: An Overview**  
*E. Chiellini*, University of Pisa, Pisa, Italy
- 10.40-11.30 **Biodegradable Products: A Positive Contribution to Sustainable Development**  
*B. Lemmes*, IBPMA-ORCA-MERLIN-Industrial Associations, Antwerp, Belgium
- 11.30-12.00 **Coffee Break**
- 12.00-12.50 **Starch-Based Biodegradable Materials: Present Situation and Future**  
*G. Floridi*, Mater-Bi, Novamond S.p.A., Novara, Italy
- 12.50-13.30 **Polymers and Plastics Production in Kuwait: Challenges and Opportunities**  
*I. Alataqi*, Kuwait University, Kuwait
- 13.30-17.30 **Lunch & Break**
- 17.30-18.20 **Synthesis and Applications of Microbial Polymers**  
*B. Hazer*, Karaelmas University, Zonguldak, Turkey
- 18.20-19.10 **On the Way to Mimic Bone Tissue: The Potential of Biodegradable Starch Based Biomaterials**  
*R. L. Reis*, University of Porto, Porto, Portugal

***September 14, 1998, Monday***

- 9.00-9.50 **Biodegradable Polymers: Biomedical Aspects**  
*E. Pişkin*, Hacettepe University, Ankara, Turkey
- 9.50-10.40 **Biodegradable Polymers and Composites: Characteristics and Uses for Implants**  
*C. Migliaresi and L. Fambri*, University of Trento, Trento, Italy
- 10.40-11.20 **Evaluation of the Compability of Biomaterials**  
*A. Motta*, Stazione Sperimentale per la Seta, Milano, Italy
- 11.20-12.10 **Coffee Break**
- 12.10-12.55 **Issues Concerning the Use of Biodegradable Materials Relating to the European Waste Legislation & Packaging Directive**  
*B. Lemmes*, IBPMA-ORCA-MERLIN-Industrial Associations, Antwerp, Belgium
- 12.55-13.40 **Hydrosoluble Biodegradable Polymeric Materials. Polyvinylalcohol. A Case Study**  
*E. Chiellini*, University of Pisa, Pisa, Italy  
 (IDROPLAST S.p.A, Montecatini, Italy)

- 13.40-17.30 Lunch & Break
- 17.30-18.15 Managing of Morphology and Properties of Degradable Biomedical Polymers and Composites  
*R. L. Reis, University of Porto, Porto, Portugal*
- 18.15-19.00 The Effect of Drawing and Annealing Conditions on the Structure and Properties of Bacterial PHB-HV Parts  
*M. M. Ghanem, M. Kadota and M. Çakmak, University of Akron, Akron, USA*
- 19.00-19.30 Plastics in Portugal: A Brief Country Report  
*O. C. Pavia and R. L. Reis, ISEP Polytechnic Engineering Institute, Porto, Portugal*

***September 15, 1998, Tuesday***

- 9.00-9.50 Biodegradable Polymers in Drug Delivery  
*R. Ottenbrite, Virginia Commonwealth University, Richmond, VA, USA*
- 9.50-10.30 Immunoprotection of Living Cells Encapsulated in the Polymeric Membrane  
*I. Lacik, Slovak Academy of Sciences, Bratislava, Slovakia*
- 10.30-11.10 The Effects of Processing Conditions on the Structure Structural Gradients Developed Injection Moulded Bacterial Parts  
*T. Yamamoto, M. Kimizu, T. Kikutani and M. Çakmak, University of Akron, Akron, USA*
- 11.10-11.40 Coffee Break
- 11.40-12.30 Degradation of Carbon-Based Polymers  
*G. Scott, North Yorkshire, UK*
- 12.30-13.10 Environmentally Degradable Plastics: Pharmaceutical and Food Grade Waste Gelatin for Agro-Industrial Application-A Case Study on ICS-UNIDO Follow-up Action  
*E. Chiellini, University of Pisa, Pisa, Italy*
- 13.10-13.40 Biodegradation of Polycaprolactone and Polycaprolactone-Based Polyurethane in Sea Water  
*K. Krasowska, A. Heirnowska, H. Janlk and M. Rutkowska, Gdynia Maritime Academy, Gdynia, Poland*
- 13.40-17.30 Lunch & Break
- 17.30-18.20 Antioxidant Control Biodegradation  
*G. Scott, North Yorkshire, UK*
- 18.20-19.00 Thermal Degradation  
*S. H. Kandil, University of Alexandria, Alexandria, Egypt*
- 19.00-19.30 Evolution Structural Hierarchy in Uni and Biaxial Deformation Fields in Polylactic Acid Films  
*Gülay Köktürk, A. Kozluca, T. Serhatkulu,, E. Pişkin and M. Çakmak University of Akron, Akron, USA*

***September 16, 1998, Wednesday***

9.00-19.30 Visit of Plastics Processing Facilities and Excursion

***September 17, 1998, Thursday***

9.00-9.50 Rational and Drivers for Biodegradable Plastics Technologies with a Case Study of the Starch-Polycaprolactone Reactive Blends  
*R. Narayan, Bioplastics Inc., Michigan, USA*

9.50-10.30 Degradable Plastics Films in Taiwan  
*S. R. Yang, Tainian, Taiwan*

10.30-11.00 Situation of Plastics in Taiwan  
*S. R. Yang, Tainian, Taiwan*

11.00-11.30 Coffee Break

11.30-12.10 Environmentally Benign Synthesis of Biocompatible Polyacetylenes  
*K. Xu, K. L. Cheuk, and B. Z. Tang*  
The University of Hong Kong, Kowloon, Hong Kong

12.10-12.50 Plastics Usage in India: Current Status  
*A.J. Varma, Polymer Science & Engineering Group, Pune, India*

12.50-13.30 Plastics in Poland  
*M. Rutkowska, Gdynia Maritime Academy, Gdynia, Poland*

13.40-17.30 Lunch & Break,

17.30-18.10 Plastics Production, Import/Export and Consumption and Potential Applications of Biodegradable Polymers in Iran  
*M. Mehrabzadeh, Iran Polymer Institute, Tehran, Iran*

18.10-18.50 Plastics Waste Management and the Position of EDPs in Slovakia  
*I. Lacik, Slovak Academy of Science, Bratislava, Slovakia*

18.50-19.30 Plastics in Syria  
*E. Qattaz and A. Kassab, Al-Baath University, Homos, Syria*

***September 18, 1998, Friday***

9.00-9.50 Standards for Biodegradable and Compostable Plastics.  
*R. Narayan, Bioplastics Inc., Michigan, USA*

9.50-9.10.20 PETKIM Petrochemicals Co. and Polymers Production in Turkey  
*R. İşler, PETKIM, Izmir, Turkey*

10.20-10.50 Solid Waste Management and Recycling in Turkey  
*Y. Karaca, Turkish Ministry of Environment, Ankara, Turkey*

10.50-11.20 Coffee Break

- 11.20-11.50 EUROKA  
*A.Çezik, G. Köksal and R. Ünsalan, TIDEB-EUROKA, Ankara, Turkey*
- 11.50-12.30 Polymer Production and Problems of Solid Waste Managment in Azerbaijan  
*A. A. Efendiev, Azerbaijan Academy of Science, Sumgait, Azerbaijan*
- 12.30-13.10 Plastics in Egypt  
*S. H. Kandil, University of Alexandria, Alexandria, Egypt*
- 13.10-13.50 Photo and Biodegradable of Polymeric Film Materials in a System of Agriculture of Tadjikistan  
*D. Khalikov, Academy of Science of Tadjikistan, Dushanbe, Tadjikistan*
- 13.50-17.30 Lunch & Break
- 17.30-19.30 Closing Session: Future Perspectives and Conslusions

**POSTERS** (September 12-19, 1998)

Computurized Infrared Analysis of Renal Stone Calculi  
*S. H. Kandil, T.A. Abou ElAzm, A.M. Gad and M.M. Abdou*  
 University of Alexandria, Alexandria, Egypt

Absorbable Polymeric Composites as Replacement for Bone Grafts  
*K. Kesenci, L. Fambri, E. Pişkin and C. Migliaresi, University of Trento, Trento, Italy*

Production and Characterization of Poly(lactide) Based Biodegradable Nonwoven Matrices  
*A. Kozluca, H. Ayhan, M. Rabaud and E. Pişkin, University of Bordeaux, Bordeaux, France*

Biodegradable Polymers and Hydroxyapatite Composites  
*E. Ural, K. Kesenci, L. Fambri, E. Pişkin and C. Migliaresi*  
 University of Trento, Trento, Italy

Manufacturing of Biodegradable Sutures  
*E.Oran, K. Abacılar and E. Pişkin*  
 Orhan Boz A.Ş. and Hacettepe University, Ankara, Turkey

***September 19, Saturday***

Before 12.00 Departures



Organizer



International Centre  
for Science and High Technology

*Trieste, Italy*

ICS-UNIDO Workshop on

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*September 12-19, Antalya, Turkey*



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Local Organizer:



Hacettepe University, Ankara, Turkey

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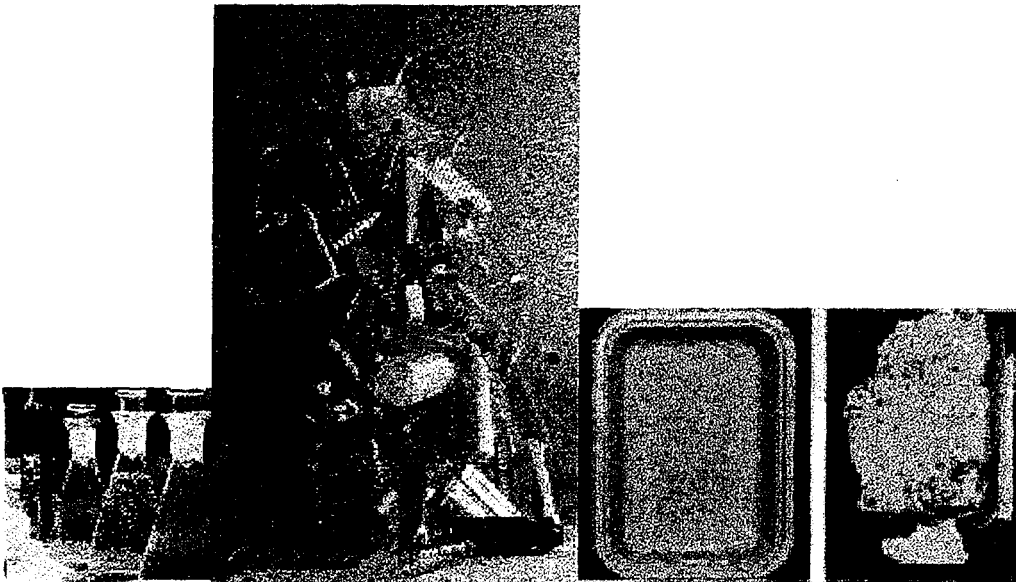
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Organizer



ICS-UNIDO Workshop on  
*Environmentally Degradable Polymers:  
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*September 12-19, Antalya, Turkey*



# *ABSTRACTS*

Local Organizer:



**Hacettepe University, Ankara, Turkey**



# INDEX

<i>Environmentally Degradable Polymers: Environmental and Biomedical aspects</i> Süleyman Sağlam.....	1
<i>Environmentally Degradable Polymers and Plastics: An overview</i> Emo Chiellini .....	2
<i>Hydrosoluble Biodegradable Polymeric Materials. Polyvinylalcohol: A case study</i> Emo Chiellini.....	2
<i>Environmentally Degradable Plastics. Pharmaceutical and Food Grade Waste Gelatinfor Agro-Industrial Applications: A Case Study on an ICS-UNIDO Follow-up Action</i> <u>Emo Chiellini</u> , El-R. Kenawy and S. Miertus .....	3
<i>Evaluation of the Compatibility of Biomaterials</i> Antonella Motta.....	3
<i>Biodegradable Polymers and Composites: Characteristics and Uses for Implants</i> <u>Claudio Migliaresi</u> and L. Fambri.....	4
<i>Biodegradable Polymers As Polymeric Drug and Druge Delivery System</i> R. Ottenbrite.....	4
<i>Managing the Performance and Properties of Degradable Biomedical Polymers and Composites-Conventional and Non-conventional Processing Method</i> Rui. L. Reis.....	5
<i>One Way to Mimic Bone Tissue - the Potential of Biodegradable Starch Based Biomaterials</i> Rui. L. Reis.....	5
<i>Degradation of Carbon-Based Polymers</i> Gerald Scott.....	6
<i>Antioxidant Control of Polymer Biodegradation</i> Gerald Scott.....	6
<i>Plastics Usage in India: Current Status</i> A. J. Varma.....	7

<i>Solid Waste Management and Recycling in Turkey</i> Yalçın Karaca.....	8
<i>Petkim Petrochemical Co. and Polymer Production in Turkey</i> Rahim İşler.....	8
<i>Eureka</i> A. Cezik., G. Koksal and R. Ünsalan.....	8
<i>Biodegradable Polymers as Biomaterials</i> Erhan Pişkin.....	8
<i>The Effect of Processing Conditions on the Structural Gradients Developed in Injection Molded Bacterial Poly(3-HydroxyButyrate-CO3 HydroxyValerate) Parts</i> M. Ghanem., M. Kadota and <u>Mükerrem Çakmak</u> .....	9
<i>Absorbable Polymeric Composites as Replacement for Bone Grafts</i> <u>Kemal Kesenci.</u> , L. Fambri., E. Pişkin and C. Migliaresi.....	9
<i>Evolution Structural Hierarchy in Uni and Biaxial Deformation Fields in Poly Lactic Acid</i> <u>Gülây Kokturk.</u> , A. Kozluca., T. Serhatkulu., E. Pişkin and M. Çakmak .....	9
<i>Production and Characterization of Poly(lactide) Based Biodegradable Nonwoven Matrices</i> <u>Ahmet Kozluca.</u> , H. Ayhan., M. Rabaud and E. Pişkin.....	9
<i>Plastics Production, Import/Export and Consumption and Potential Applications of Biodegradable Polymers in Iran</i> M. Mehrabzadeh.....	10
<i>Biodegradable Polymers and Hydroxyapatite Composites</i> Ebru Ural., <u>K. Kesenci.</u> , L. Fambri., C. Migliaresi and E. Pişkin .....	10
<i>Polymers &amp; Plastics production in Kuwait, Challenges and Opportunites</i> I. Alatiqi.....	10
<i>Synthesis and Applications of Microbial Polymers</i> Baki Hazer.....	10
<i>Polymer Production and Solid Waste Management in Azerbaijan</i> A. A. Efendiev.....	11
<i>Environmentally Benign Synthesis of Biocompatible Polyacetylenes</i> Kaitian Xu, Ka Leung Cheuk, and <u>Ben Zhong Tang</u> .....	11
<i>Degradable Plastic Films in Agriculture in Taiwan</i> Yang Shaw-rong.....	11

<i>Biodegradation of Polycaprolactone and Polycaprolactone - Based Polyurethane in Sea Water</i> K. Krasowska, A. Heirnowska, H. Janlk* and <u>M. Rutkowska</u> .....	11
<i>Plastic waste management and the position of EDPs in Slovakia</i> Igor Lacik.....	12
<i>Immunoprotection of living cells encapsulated in the polymeric membrane</i> Igor Lacik.....	12
<i>Starch-Based Biodegradable Materials: Present Situation and Future Perspectives</i> Catia Bastioli, <u>Giovanni Floridi</u> .....	12

## Environmentally Degradable Polymers: Environmental and Biomedical Aspects

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As we are approaching a new millennium, there are drastic changes all over the world in regards to environmental issues. Destruction of natural resources and environmental problems of our planet have taken on even greater dimensions, and our understanding of the concept of environmental problems have greatly improved. It is now recognized that the environment must be viewed in its interactions with development, and that we have to achieve a sustainable development for our common future. In this sense, there is a global obligation of environmental justice placed upon the present generations, which is owed to posterity. International co-operation and solidarity are needed today more than ever to prevent over-exploitation of natural resources and environmental degradation and to achieve a rational environmental management that would enable sustainable development. The "Only One Earth" concept has now been widely accepted understanding that the humanity shares common environmental values and posterity will share a common future; in this sense, the interactions between development and the environment must be taken into consideration in all aspects at the national, regional and global levels.

The idea of sustainable development views the world as a single market, and requires countries to have their shares in this market according to their present structures. However, there are important obstacles to the implementation of such a philosophy, like disparities in levels of development bilateral and multilateral agreements presently in effect, differences in economic systems of the countries protection afforded to certain sectors, and foreign trade policies. The attainment of sustainable development on a global scale depends, on the first place, upon the attainment of a certain level of development by the countries in transition. In this connection the basis of an international economic policy should be the provision of political, technical and financial support to contribute to the development of these countries.

Although it is true that every section of societies has a common interest in environmental protection and that environmental destruction will produce results affecting the entire world, the development of a sound global approach in the long run requires the adoption of this policy by the countries in such a manner as not to hinder their development efforts, and in line with their levels of development. We believe that this responsibility must be reasonably shared, by being open to the desired global co-operation.

The most effective way to protect the environment and to avoid pollution is through measures taken in advance to prevent degradation. To do this, experience and accumulation of knowledge in environmental management as well as investment i.e. material and financial sources are necessary. When this phenomenon is viewed from the perspective of developed countries and countries in transition, it may be assumed in general that the latter are at a two fold disadvantage as compared to the former. In the countries in transition, scientific, technical, technological, human and other factors impose limitations on a sound environmental management. It is obvious that the countries in transition, where environmental problems have often emerged more recently than in the developed countries, have yet to learn the most effective use of these resources for environmental purposes, as compared to the developed countries who accumulated some experience in coping with these problems. This offers an opportunity of co-operation between the two groups of countries. The transmission of the experience acquire by the countries in transition to the others will enable this countries to take action more swiftly, without wasting human and financial resources and without repeating the mistakes of the developed countries. This need has been

expressed at certain regional and other international platforms, and some positive efforts have already been started. For example, such activities are being carried out among the OECD countries and are widened so as to include also the Eastern and Central European Countries.

Similar to other countries in transition, Turkey is experiencing rapid population growth, a very rapid urbanization process, and modernization especially in urban areas. In parallel, solid waste management, which is one of the important environmental aspects is becoming extremely complex to be solved. Solid wastes formed both in the daily lives and in industrial and commercial activities, which is mostly going to landfill, is rapidly growing especially in urban areas. It is estimated that about 20 million tons of solid waste is forming in a year in Turkey. The question of disposal of solid waste and reuse without damaging the environment or in other terms solid waste management is a difficult one to be answered. Because there is a need for serious studies on the amounts, composition, storage, collection, transportation and dumping of solid waste especially in urban areas exiting, and also can be expected in future years.

Today, polymers are used in the production of a wide variety of materials for diverse applications. The expectations in the 21st century for polymeric materials demand are in favor of a 2 to 3 fold increase of polymeric materials production as a consequence of the increase in their consumption especially in the developing countries. In the next couple of decades the overall production of polymeric materials is expected to reach a value as high as 350-400 million tons per year. Therefore a one order of magnitude jump in the polymer consumption, with respect to the present annual level can be envisaged for those countries with a per capita share lower than 5-10 kg, once the living standards of the developed countries is reached.

The high production and consumption of polymeric materials have already brought in sight the environmental aspects of polymeric waste which has promoted all over the World a great deal of actions aiming to provide adequate solutions for minimizing this negative impact. There are constrains and regulations already operative or to be issued in the near future dealing with this subject. Burial in landfill sites, incineration with energy recovery, and mechanical or chemical recycling are presently adopted alternative technologies available for the management of polymeric waste. Use of biodegradable polymers which may replace the conventional commodity polymers in those segments in which other waste management approaches are difficult to utilize and/or uneconomical, have been considered as one of the novel alternative approaches. In this approach it is expected that the materials made of biodegradable polymers stay stable during processing, storage and use, but do undergo degradation under environmental conditions in the waste. One of two main objectives of this ICS-UNIDO workshop is to discuss biodegradable polymers used mainly in commodity polymeric materials by focusing on environmental aspects.

Polymers have also being utilized very widely as biomaterials in medicine to replace a diseased or damaged part of the body, to assist in healing, to improve function, to correct cosmetic problems, to aid treatment, and for diagnosis. In these applications, polymers do come into contact with the soft and/or hard tissues or the cardiovascular blood system, or with both. Non-biocompatible materials may be rejected and also may cause important side effects. Therefore, in addition of the required properties depending on their final use, polymeric materials must meet certain criteria and regulatory requirements before they can be qualified for use in biomedical applications. Both nondegradable and biodegradable polymers are used as biomaterials in different forms. Biomaterials made of biodegradable polymers, mainly temporary artificial implants, are designed to degrade in

vivo in a controlled manner over a predetermined period, which eliminates a secondary surgery to remove the material after serving their intended purpose. The second main objective of the proposed workshop is to discuss biodegradable polymers used in more specialty polymeric materials, namely in biomaterials by focusing on biomedical aspects.

## Environmentally Degradable Polymers and Plastics: An Overview

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Synthetic and semisynthetic polymeric materials were originally developed for their durability and resistance to all forms of degradation including biodegradation. Special performance characteristics are achieved in items derived therefrom through the control and maintenance of their molecular weight and functionality during the processing and under items operative conditions. The polymeric materials had been and are currently widely accepted because of their ease of processability and amenability to provide a large variety of cost effective items that helped enhance the comfort and quality of life in the modern industrial society. However the above quoted features, that make the polymeric materials so convenient and useful to the human life, have contributed to create a serious plastic waste burden, sometimes unfairly oversized by media because of the visible spreading of plastic litter in the environment and the heavy contribution to landfill depletion due to the unfavorable weight to volume ratio of plastic items that is in average 1 to 3. On the other hand the expectations in the 21st century for polymeric materials demand are in favor of a 2 to 3 fold increase production as a consequence of the increase of the plastics consumption in developing countries. Indeed a one-two order of magnitude jump in the plastics consumption with respect to the present annual level of 1-10kg procapita can be envisaged for those countries once the living standards of industrialised countries will be approached.

The design, production and consumption of polymeric materials for commodity and specialty plastic items have certainly to face all the constraints and regulations already in place or to be issued in the near future, dealing with the management of primary and post-consumer plastic waste. In this connection the formulation of environmentally sound degradable polymeric materials and relevant plastic items will constitute a key option among those available for the management of plastic waste. The competition with the presently adopted technologies such as burial in landfill sites, incineration with energy recovery and mechanical or chemical recycling is expected to be strengthened, even though one may predict that all of them will coexist with an appreciable decrease of landfilling practice and the introduction of the new concept of prevention that should help to rationalize the production and management of plastic waste. The technologies based on recycling, including also the energy recovery by incineration, will be flanked by the increasing option of environmentally degradable plastics, that should replace the conventional commodity plastics in those segments in which recycling is difficult and heavily penalized from an economical standpoint. An overview on environmentally degradable polymers and plastics cannot therefore be treated outside of the framework of the global issue related to the waste production and relevant management. The position held by environmentally degradable plastics will be analyzed in terms of the development levels so far reached and of the future perspectives. It is worth mentioning that a major aspect that has attracted the attention of plastic manufacturers, polymer scientists, and public officers, is represented by the establishment of definitions comprising all the possible

categories of environmentally degradable polymers and plastics, together with suitable standards and testing protocols.

The nature and fate of the degradation products constitute another crucial point for the acceptance of environmentally sound synthetic polymeric materials undergoing degradation under specific environmental conditions. As a conclusion of the analysis carried out in the presentation, no universal standards and testing protocols can be selected so far to assess the environmental degradability of polymeric materials. From case to case, specific environmental conditions and relevant test protocols have to be defined implying a knowledge of adequate physical parameters and microbial strains eventually utilized in the evaluation and validation tests.

## Hydrosoluble Biodegradable Polymeric Materials. Polyvinylalcohol: A Case Study

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Environmentally degradable polymers have been receiving increasing attention for the preparation of plastic items that are supposed not to create environmental burden once they enter the stream of post-consume items. Packaging for single doses items in hygiene, agricultural and fish farming applications is becoming more and more diffused as driven for safety and ecological reasons. PVA can be considered as the only true biodegradable synthetic polymer consisting of a carbon backbone. Evidences of this feature have been reported since the early thirties in studies carried out with single microorganisms and symbiotic mixed cultures. In the early seventies biochemical pathways have been designed by assuming that hydroxyl groups are enzymatically oxidized to p-diketones or a-keto groups and subsequently hydrolyzed with the ultimate fission of the carbon-carbon bond. Nevertheless due to the nowadays consolidated and future consumption of PVA based formulations, investigations on the fate of the post-consume items have to be performed both in liquid and solid culture, according to the several procedures aimed at closely reproducing the conditions of natural ecosystems or waste treatment facilities.

In this context a careful extensive investigation on the biodegradability of different commercial PVA-based blown films produced by blown extrusion was undertaken by means of respirometric tests carried out both in liquid and solid cultures simulating sewage sludge, composting and soil burial conditions. Effectiveness of microbial populations present in the environmental matrices utilized as inocula, was also investigated in liquid cultures by iodometric evaluation of PVA concentrations. Results obtained evidenced a clear effect on biodegradation rate and extent, attributable to both environmental conditions and microbial populations. In particular, PVA-based films and PVA undergo a very limited mineralization extent in solid cultures (composting and soil burial) whereas high rate of biodegradation were observed in liquid cultures in the presence of paper mill sewage sludge and selected PVA-degrading mixed inocula. Nevertheless it remains yet unclear if the limited biodegradation of the vinyl polymer in soil and composting can be attributed to the absence of PVA-degrading microorganisms in the utilized environmental conditions or rather to unpaired interactions with organic and inorganic components analogous to those that hinder humus and polysaccharides biodegradation in soil. The industrial manufacturing of blown extruded films based on PVA formulation will be also thoroughly analyzed as a typical case study relevant to the production and consumption of environmentally degradable plastic items.

**Environmentally Degradable Plastics.  
Pharmaceutical and Food Grade Waste Gelatin  
for Agro-Industrial Applications: A Case Study  
on an ICS-UNIDO Follow-up Action**

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Plastics have gained a unique position in materials technology for a number of reasons. Initially they were used as substitutes of paper, glass and metal because of their better physical properties and because plastics are more economical than metals, wood and glass in terms of manufacturing costs, weight to strength ratio, and cost/performance convenience. Plastics have also achieved a dominant position in agriculture and horticulture, which has merited the new description 'plasticulture' to describe the use of plastics in greenhouses, tunnels, irrigation in protective covers for crops and mulching films. Plastic waste may represent however a serious concern for the environment because of the recalcitrance of most of the synthetics to microbial attack. Recent estimates indicate that more than 1-3 kg/person of municipal solid waste (MSW) is daily generated in industrialized countries. The average content of plastic waste in MSW is comprised between 5-10 % by weight corresponding to 20-30 % by volume. This makes polymer waste management an urgent problem, needing environmentally compatible and friendly solutions, both on short and long term bases.

It is generally recognized that there is no single, simple solution to waste management but there is a fairly broad range of options comprising either reduction of the amount of material entering the waste stream and/or dealing with its ways of disposal. Since plastic waste has caused serious, but often emotionally exaggerated environmental concern, there are nowadays increasing demands to develop environmentally degradable polymeric and plastic materials. The search for biodegradable alternatives to stubbornly bioresistant thermoplastics has led to the exploitation of the complementary properties of natural and synthetic polymers as blends, block copolymer, or graft copolymers.

Proteins of vegetal-animal origin and starch are of particular interest since these biopolymers have no adverse impact on human or environmental health. Collagen is an important constituent of the supporting structures of both vertebrates and invertebrates. In mammals, gelatin represents the most abundant body protein forming the major constituent of skin, tendon, cartilage, hides, bone and connective tissue. It has been estimated that collagen comprises about 30 % of the total organic matter in mammals with a content of 60 % in proteins. Gelatin is a partly denatured collagen and is widely used as biological glue in surgical operations, in various industrial applications such as food products (stabilizers, thickeners, texturizers, meat packaging and other food processing), pharmaceutical technology (hard and soft gelatin capsules and gelatin coated tablets) and photographic films. However, gelatin waste generated in the different manufacturing processes including tannery, butchery and pharmaceutical industry may constitute a great concern for the environment due to strong swellability in water medium at room temperature which in turn may cause problems to the drainage system and water solubility at higher temperature (~ 40 °C) which consequently present a more serious problem in that they are likely to increase the strain on the sewage disposal system. Also, due to the high carbon and nitrogen content, a high oxygen demand is required once the waste gelatin may reach the sewage drainage system and waste water treatment plants.

The use of mulching films in agriculture, has led to a very substantial increase in the yields of soft fruits and vegetables in many areas all over the world, because plastics films not only helps to increase the temperature of the soil, but also reduce the usage of irrigation water and fertilizers with consequential beneficial economical and environmental returns. The disposal of agricultural mulching films, can represent a key in the economy of the overall productive cycle, primarily caused by the advent of automated harvesting. Cropping equipments are often rapidly put out of action by plastic based litter on the surface of the soil and residual undergraded plastics, once buried, may survive for long time and interfere with the root growth of subsequent crops. The intensive and costly labour to remove such debris from the fields by manual collection in large-scale plasticulture, may result in a drastic reduction of the benefits connected with the increased crop yields.

In the present contribution, we report on a case study that originated as follow-up of the ICS-UNIDO TC on Environmentally Degradable Plastics held in Egypt in Summer 1997. In particular the preparation and characterization will be described of biodegradable blends and composites based on waste gelatin, produced by an Egyptian pharmaceutical Company and other natural or synthetic waste materials and designed for the fabrication of environmentally sustainable mulching films, and soil conditioners. Those films, thanks to the inherent biodegradability properties and the presence of proteins nitrogen (12-15% by weight), could be classified as self fertilizing mulching films.

#### Evaluation of the Compatibility of Biomaterials

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As agreed in a consensus conference, the term "Biocompatibility" indicates: "The ability of a material to perform with an appropriate host response in a specific application". In this respect, it appears clear that, even if a material is not toxic or not toxic leachables diffuse out from it, this constitutes only one of the conditions leading to the real biocompatibility of a material. Surgery takes today advantages from the use of biomaterials, for biodegradable or biostable implants as well, for permanent devices and soft and hard tissue augmentation, or total artificial internal organs. However, there are risks and failures in each application as a result of undesirable biological interactions.

The Medical Device Directive (MDD) contains essential requirements for the chemical, physical and biological properties of medical devices. These are explained in Annex I of the directive and call special attention to choice of materials, their toxicity, and compatibility with biological tissues and fluids. The device manufacturer is responsible for ensuring conformity with the essential requirements, and depending on the device classification, a notified body may need to verify this information.

The practical application of the essential requirements comes in the form of harmonized standards. These standards that CEN (Commission for European Standards) adopts and publishes in the Official Journal of the European Communities. If the manufacturer complies with a harmonized standard, conformity with the MDD essential requirements is presumed. For biocompatibility the standard that CEN expects to adopt is ISO 10993.

The US FDA has required testing to the Tripartite Agreement, which has similar requirements to ISO 10993. In fact, ISO 10993 has fewer requirements in many cases. The FDA is expected to adopt ISO 10993 in place of the Tripartite Agreement in the near future.

The standard revolves around a matrix that relates device category to recommended tests. Devices are categorized based on patient contact and contact duration. The extent of these two determining factors decides which tests are applied. The

standard is meant as a guide and allows for interpretation depending on the use of the device. Patient contact is broken down into surface (external) devices, externally communicating devices, and implant devices. The surface device has three subcategories of intact skin, intact mucous membrane contact, and breached surface contact. Externally communicating devices are broken down into tissue/bone, indirect blood path, and circulating blood path. Implants are divided by tissue/bone and blood. Each of these subcategories is broken down by duration.

Depending on which category the device falls into there are up to 12 tests recommended. Nine of these are short term and three are long term. The long-term tests are all *in vivo* tests, that is they require animal implantation. Three of the short-term tests are *in vitro*, that means done in a test tube, and the balance are *in vivo*. Testing can be done on either materials or finished devices. proper sampling is required and is handled on a case by case basis.

The *in vitro* tests are judged on a pass/fail standard while many of the long-term *in vivo* tests require pathological review by qualified technical expert. In conclusion, many steps are required in the development of a medical device from the concept phase to full-scale production. The actual number of steps may vary according to the novelty and complexity of the finished product. However, the development process is nearly always multidisciplinary and includes checkpoints for testing and validating the new device and its component materials aside from functionality that are of key importance in the development process: chemical, physical and biological.

### Biodegradable Polymers and Composites: Characteristics and Uses for Implants

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The use of biodegradable polymers for the fabrication of biomedical implants offers at least two advantages, i) elimination of the need of a second surgery to remove the prosthesis after the healing of the tissues, and ii) possibility of triggering and guiding the tissue regeneration via the degradation of the material.

Due to the above benefits, the demand of biodegradable polymers has progressively increased in the past years, and several biodegradable polymers based devices and prostheses have been proposed. Most of these systems are based on polyesters, such as polylactic or polyglycolic acids, or their copolymers, that undergo to hydrolytic degradation once implanted.

Degradation kinetics depends on many factors, i.e. nature of the polymer, its morphology, size of the device, fabrication and sterilization processes, the implant site... For instance, while degradation of polyglycolic acid occurs in three-four weeks, polylactic acid devices can last for much longer time, even up to three-four years, in the case of high molecular weight and highly crystalline polymers.

The processing condition of the biodegradable polymer can play a very important role on its final characteristics, being some of them sensitive to thermal degradation or resulting the hydrolysis catalyzed by temperature, even if in presence of very small amounts of water. Furthermore in dependence on the type and intensity of the sterilization procedure (ethyleneoxide, beta-rays, gamma-rays), various degradation phenomena occur and determine an anticipated/premature reduction of properties during application with respect to the expected values.

In the case of semicrystalline polymers, some properties can be properly modified throughout monoaxial drawing, so obtaining, for instance, fibers with higher mechanical properties or films with piezoelectric properties and claimed osteogenic properties.

In order to favourite osteogenesis, composites with ceramic osteogenic powders have been also prepared.

For many application, when devices or prostheses have to bear loads, i.e. in orthopedics or maxillofacial surgery, mechanical properties of polymers are not sufficient, so that composite systems have been developed with fibers reinforcing the matrix, with a gain bounded from the moderate mechanical properties of the biodegradable polymers derived fibers.

The lecture will review the properties and the applications of biodegradable polymers and composites used for the fabrication of biomedical implants, paying special attention to the aspects reported above.

### Biodegradable Polymers As Polymeric Drug and Drug Delivery System

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There is a major trend to use biodegradable polymer systems in the area of polymeric drugs and drug delivery for several reasons. These include eventual elimination from the blood compartment through the renal system after intraperitoneal injection and the degradation of implants in the tissue which obviates the need for surgical removal of long term delivery systems. Although the advantages of biodegradable systems are well documented the number of polymers that are viable candidates for this type of application is limited. Until recently, the designers of drug delivery systems used readily available polymers, which had been developed for other purposes. Since then it was found that polymers consistently behave different *in vivo* than *in vitro*. The most thoroughly evaluated polymer system is based on the lactide and glycolide polyesters and more recently the polycaprolactone system. The parameters evaluated include the kinetics of degradation under a variety of conditions, biocompatibility and the association with the incipient to be delivered. The excipients first delivered were tetracycline for periodontal disease, norethisterone for contraceptive estrogen as a growth promoter and various vaccines. The polyorthoester systems were found to confine their degradation predominantly to the surface of the implant simplifying the kinetics which usually involves both surface erosions as well as diffusion from the inner core of the delivery device. Another ester type system involved polyanhydrides. They were developed to undergo degradation much faster than the traditional ester functions and were specifically designed for delivery of anticancer drugs in the cranial compartment. Two unique polymer systems are the polyphosphazenes, which are essentially inorganic and the pseudopoly(amino acids). These systems can be used as degradable devices or as polymeric drug carriers whereby the drug is linked to the polymer by means of a degradable functional group. Steroids, imidazolyl and anesthetics have been conjugated to polyphosphazene polymers and found to exhibit interesting delivery profiles. Of course natural polymers are prime candidates as biodegradable materials for drugs carriers and matrix devices. These include proteins (i.e. albumin and collagen) and polysaccharides (i.e. alginates and chitosan). In addition, the self assembly and self aggregate systems, which can encapsulate drugs in their inner core or interstitial in physically bonded, rather than chemically bonded, microparticles which dissociate in bioenvironments are attracting considerable interest. These and other biodegradable systems will be discussed.

## Managing the Performance and Properties of Degradable Biomedical Polymers and Composites- Conventional and Non-conventional Processing Methods

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The possible applications of biodegradable polymers strongly depend on their mechanical performance, water-uptake capability and correspondent degradability. The development of new materials and/or innovative processing routes to produce biodegradable parts exhibiting an enhanced mechanical performance may broaden the field of application of these materials. This will, eventually, increase the installed capacity for the production of these polymers, leading to the aimed goal of approaching their prices to those of standard commodity plastics.

This lecture describes the application of different techniques (twin screw extrusion, conventional and non-conventional injection moulding, production of porous materials and structural foams) to process highly thermal and water sensitive degradable polymers. Initially, the conventional injection moulding parameters that should be controlled, and their effects on the attained mechanical performance are described. Also the effects of compounding techniques on the morphology and properties of particle reinforced degradable polymers are discussed. Biaxial rotating drum (RD) and co-rotating twin-screw extrusion (TSE) compounding are compared. Special attention is given to biomedical applications. Hydroxylapatite (a bone like ceramic - the major inorganic constituent of human bone) reinforced starch based thermoplastic composites are used to illustrate the typical results that may be obtained. The studied biodegradable composites are based on corn starch, ethylene vinyl alcohol, and cellulose acetate blends. The potentialities of applying design of experiments (DOE) methods and ANOVA statistical tools for optimising the materials processing and respective properties are briefly described. The possibility of employing titanates and zirconates coupling agents to further improve the composites mechanical performance is also addressed.

The lecture also reports on the use of non-conventional processing technologies, such as *shear controlled orientation in injection moulding* (Scorim) to further enhance the materials mechanical behaviour, and induce anisotropy into the mouldings, with the aim of copying bone structure. Ways to optimise the materials processing dependent morphology are discussed. The final goal is to copy bone structure and attain the aimed mechanical performance - matching that of human bone. Nevertheless, it will be clear that these methodologies may equally be applied with great success to polymers being used on environmental degradable applications. On both cases, the materials formulation, the selected processing routes, the amount of filler, and the control of the morphology development during processing, have a direct effect over the correspondent mechanical properties. The integrated optimisation of all these variables testifies that these composites can be an effective alternative to the biodegradable systems currently used in clinical practice. The use of Scorim processing, associated to a proper compounding by TSE, allows for the elaboration of mouldings with a controlled anisotropy (as that in bone). It is possible to obtain simultaneously higher values of stiffness, strength and ductility (as compared to conventional injection moulding), and to match the mechanical properties of human cortical bone.

Finally, the development of ways for producing materials with a compact surface and a porous core, copying the typical structure of human (cortical + trabecular) bone, is presented. The main processing routes are based on traditional injection moulding on which carboxylic acid based masterbatches are employed to manage the desired morphological development. Also biodegradable foams (fully porous materials) may be produced by innovative blowing techniques, including microwave based methods. Possible applications of the developed materials in orthopaedics, are bone replacement and fixation, as well as scaffolds for the tissue engineering of bone.

## On the Way to Mimic Bone Tissue - the Potential of Biodegradable Starch Based Biomaterials

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There is a need for the development of new biodegradable composites both for being used in orthopaedic temporary applications (bone replacement/fixation), and as adequate tissue engineering scaffolds. The main constraints for the introduction of novel systems into this field are their mechanical behaviour, degradation kinetics and biocompatibility. This lecture describes an oriented research work that proposes alternative load-bearing biodegradable systems, for being used in hard tissue replacement, and as adequate 3D-architectures to be utilised as scaffolds for the tissue engineering of bone. The newly developed starch based thermoplastic composites can be processed into parts with optimised morphologies and mechanical properties, as reported on the previous lecture. These polymers present a combination of properties that foresees a great future for its application instead of the currently clinical used biodegradable polymers.

The studied systems are based on corn starch blended with ethylene vinyl alcohol or on corn starch blended with cellulose acetate. Both matrixes were reinforced with hydroxylapatite (HA). The degradation (weight loss, water-uptake, structural changes and alterations on the tensile properties) of the polymers and the composites was studied in an Hank's balanced salt solution with or without bovine serum additions, and on extractions with cell culture medium. The problems related with this type of tests and the relevance of the attained data are addressed in detail. The materials formulation, the selected processing routes, the amount of filler, the control of the morphology development during processing, and the addition of proteins have a direct effect over the in-vitro degradation behaviour. The developed biodegradable composites are (or can be made to be) bioactive, i.e. they can grow (or be made to grow), on an extracellular fluid, a calcium-phosphate (Ca-P) layer on its surface (or porous cell walls) that will promote their in-vivo bone-bonding behaviour. Experimental procedures for the in-vitro bioactivity testing of the novel materials were developed on a solution simulating the human blood plasma. The problems related to setting-up this type of testing and the typical data that can be achieved is reported. It is shown that the starch based polymers can induce, in certain conditions, by themselves the formation of a Ca-P layer on its surface, indicating that they might mineralise and present a bone-bonding behaviour in-vivo. Furthermore, Ca-P coatings can also be nucleated and grown, in a simulated body fluid (SBF), by an adapted biomimetic route. It is possible not only to produce a Ca-P bone-like layer at the surface of compact materials (polymers and composites) but also on the cell walls of porous 3D-architectures.



The lecture will also describe the extensive biocompatibility testing that is required to try to introduce a new biodegradable system into the biomedical field. Standard cytotoxicity trials, including MEM extraction, MTT assays and direct contact tests, using human fibroblasts and mouse lung cell lines are reported. All tests were carried out according to GLP practices in certified Labs. The problems associated to the testing of biodegradable polymers are discussed, and possible ways for the in-vitro simulation of their long-time implantation presented. The behaviour of the materials when in contact with human osteosarcoma cells (HOS, osteoblastic like cells) was also studied. The in-vivo tissue reactions were analysed in an intramuscular and intracortical bone implantation goat model. Some hints on the adequate research approach and interpretation of the obtained results will be presented, showing the great potential of the starch based polymers and composites for the proposed applications. The results obtained on the starch based polymers prove their biocompatible behaviour, and their in-vivo degradation and bone-bonding behaviour.

### Degradation of Carbon - Based Polymers

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Interest in new biodegradable polymers and particularly those based on renewable resources has sharply increased in recent years. This has tended to obscure the biological benefits of the commercial plastics and particularly of the polyolefins. The Technological and ecological advantages of the polyolefins must be the base - line for the from which to assess the urge to return to natural products as the basis of packaging materials. The advantages of synthetic packaging polymers and in particular the polyolefins are as follows <sup>1</sup>.

1. Polyolefins are manufactured on a very large scale with minimal land utilization and are very cheap. They stand in contrast to polymers based on natural products which are more expensive to produce and require large areas of land for the production of raw materials and frequently cause damage to the ecosystem when they are harvested (e.g. cellulosic polymers from trees). It has been estimated that to replace plastics by cellulose in packaging would require land with an area six times that of the US state of Tennessee <sup>2</sup>. Similar arguments apply to the production of poly(hydroxyalcanoates) (PHA) from natural sources <sup>1</sup>.
2. Energy utilization during the manufacture of plastics beverage containers is only 4% of that of aluminium, 16% of that steel, 6% of that of glass and 60% of that of paper <sup>2</sup>. Polymers derived from natural products are not more environmentally friendly than those made from oil since they both consume oil during their manufacture.
3. Gaseous polluting by - products (e.g. SO<sub>2</sub>, NO<sub>x</sub>) are lower for polyethylene than for cellulose. Furthermore, pollution of waste water for PE is less than 1% of that for paper <sup>2</sup>.
4. Hydrocarbon polymers have better water - barrier properties than water absorbing biologically - based polymers. Consequently they protect foodstuffs from biological attack more effectively and longer.
5. Because of their low bulk density, polyolefin packages require much less energy in the transport of commodities such as milk and soft drinks. It has been shown that in a major city such as Munich, if glass rather than plastics was used in the delivery of milk an additional 240,000 liters of diesel fuel would be required daily <sup>3</sup>. The ecological deficiencies of the hydrocarbon plastics appear only when their ultimate disposal is considered. Although hydrocarbon polymers can be incinerated with energy recovery <sup>4</sup> thus conserving oil

resources, incineration is viewed with suspicion by the general public in Europe.

Materials recycling by reprocessing is in general more expensive than incineration and involves the input of considerably more energy because of the need to collect plastics from areas distant from the reprocessing plant and essential cleansing processes cause water pollution. Mixed plastics, particularly when contaminated with foodstuffs or transition metal ions give rise to much inferior secondary products which can not compete with those made from virgin polymers <sup>4</sup>. It is normally economically viable to use them as fuel. Composting is now recognised in international protocols as a recycling process. The biomass produced is important to the growth of new plant life and the coproduct, carbon dioxide returns to nature's carbon cycle. Some biological polymers such as cellulose and starch are returned to the biological cycle very rapidly but regular carbon - based plastics do not biodegrade rapidly enough in municipal or farmyard compost to be disposed of as bioassimilable wastes. However, after peroxidation, for example by heat or in sunlight the hydrocarbon polymers are broken down to biodegradable low molecular weight carboxylic acids and alcohols which are rapidly converted to biomass in contact with the soil.

Hydrocarbon polymers do not normally biodegrade in compost or as litter because they are formulated with antioxidants in order to resist environmental degradation. However, antioxidants have been developed which protect the polymer during manufacture and in service but which invert to become prooxidants during disposal in biotic environments <sup>4</sup>. The chemistry and applications of this technology will be discussed in the next lecture.

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### Antioxidant Control of Polymer Biodegradation

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Antioxidants protect polymers from peroxidation and physical deterioration <sup>1</sup>. They act either by interrupting the peroxidation chain - reaction ( chain - breaking mechanism ) or by removing or retarding the action of initiating species such as hydroperoxides transition metal ions ( preventive mechanism ). Both chain - breaking and preventive antioxidants may act catalytically and combinations of the two classes are synergistic <sup>1</sup>. The most important sub - group of the preventive antioxidants are the peroxide decomposers. The transition metal dithiocarbamates are members of this class and are converted to sulphur acids by hydroperoxides. Sulphur acids are catalytic peroxide decomposers and vary in effectiveness depending on the nature of the transition metal ion <sup>2,3</sup>. By combining different transition metal ions with different prooxidant activity, it is possible to completely suppress damaging peroxidative reactions during processing and in service but when the prooxidant reactions are 'triggered' after discard either by sunlight or by heat in compost, they initiate the rapid formation of low molecular weight biodegradable products. The 'light - trigger' mechanism is now used

commercially in the manufacture of polyethylene mulching films with controlled stability, polypropylene baler twines which degrade after a period of about one year and encapsulated fertilisers which release the nutrients at a controlled rate with reduction in pollution of rivers and lakes.

Polyethylene mulching films offer considerable economic benefits to farmers as a result of increased crop yields and an earlier entry to the market. They also reduce water and fertiliser usage. The main disadvantage of regular polyethylene is that the non-degradable residues have to be manually collected at the end of the growing season; otherwise they interfere with subsequent root growth when ploughed into the ground photo biodegradable polyethylene mulching films which fragments at the time of harvest, thus eliminating clogging of automated harvesting equipment, is subsequently bioassimilated to become part of the ecosystem. Photo-biodegradable mulch thus offers the farmer additional economics due to lower labour costs since the waste plastic does not need to be collected and disposed of by incineration<sup>3,6</sup>.

Photo-biodegradable polyolefins are also being used increasingly in the control of other types of litter. A notable example is the use in the USA of polypropylene baler twines which are programmed to fulfill their function normally but which fragment and biodegrade after one year<sup>3,6,7</sup>. The residual polymer resulting from the use of PE in mulching films has been shown by Arnaud et al.<sup>8</sup> to be bioassimilable and Kawai et al.<sup>9</sup> have similarly shown that the empty shells remaining from encapsulated fertilisers biodegrade naturally in the presence of soil microorganisms. The present trend is to design polymers for ultimate disposal<sup>6,10</sup>. Products which end up in sewage have to biodegrade to CO<sub>2</sub> within days or weeks and the synthetic polyesters generally satisfy this requirement. Packaging materials have to remain strong for weeks or months but should fragment and begin to biodegrade to biomass within weeks of outdoor exposure or on incorporation into compost. Agricultural plastics (mulching film or packaging) have to survive in the environment without loss of mechanical properties for months or even years. They are then required to fragment rapidly and biodegrade. The time to complete mineralisation is much less important in the case of compost or soil than in the case of sewage provided that no plastic accumulate in the environment. Photo-biodegradable polyolefins fulfill these criteria ideally.

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## Plastics Usage in India : Current Status

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India's per capita consumption of commodity plastics is around 1.8 kg, and the Indian plastic industry's steady growth of 16% is fuelled by a growth in GDP and the increasing ethylene capacity. The ethylene capacity is likely to grow from 0.5 million tonnes per annum (mtpa) to 2.5 mtpa by 2000 A.D. Between 1994 and 1996, imports accounted for 31% of the plastic industry's total consumption. The export of plastics fetched US \$484 million in 1995-96, and the target is \$ 2 billion by 2001-2. In addition, the Plastic and Linoleum (Carpets) Export Promotion Council has a target of \$ 100 million. The chief markets are UAE, Saudi Arabia, UK, and Bahrain. Of the total plastic consumption, the packaging industry consumes 25%, the water management sector 24 %, and the infrastructure sector 30%. Shortages are felt in all the commodity plastics (PE, PP, PS, and PVC). With production and consumption rising, India is estimated to produce about 2 mtpa of plastics waste each year, 60% of which enters the recycle industry (in Europe only 7% of the plastics are recycled, and in Japan the figure 12%). Over 1000 tonnes of plastics waste are received for sale to reprocessors every day in plastic waste collection centres in various parts of the country, where it is further segregated. Of this, between 60-80% get reprocessed. Recycling is done mostly in the unorganized sector. To manage these ever increasing volumes of waste, India would require upgradation and diversification of recycling capacity and technology. There are 20,000 plastics processing units in India, of which 85% are in the small scale, and 15% in the medium sector. The processing capacity is over 4 mtpa, of which only 50% is currently used. In addition to carry bags, toys, footwear, and other such items. 5% of the molded luggage industry in India is based on recycled plastic waste.

A national plastic waste management task force has been constituted by the government of India to prepare an action programme for management of plastic waste in India and recommend incentives, penalties and levies for checking the growth of plastic packaging waste. The Ministry of Environment and Forests, Government of India, has recommended stern guidelines for recycling plastic wastes, and rules have been framed by the Bureau of Indian Standards. Recycled plastics have been prohibited from manufacture of container for storing, carrying, or packaging food items, and water bottles. The notification specifies that polyethylene bags made of virgin plastic have to be at least 20 microns thick, and those from recycled material at least 25 microns thick. This would be an incentive for rag-pickers, and therefore littering will be avoided. Also to avoid dangerous waste like syringes and surgical gloves, the government plans to initiate a countrywide awareness programme on the growing menace of plastics. They are also setting up an Indian Centre for Plastics in Environment (ICPE), which will work on upgrading recycling technology. This comes in the wake of a strict warning from the ministry, asking the industry to self-regulate the recycling process. The Bureau of Indian Standards now requires manufacturers to mark their polyethylene bags with one of the suggested symbols, indicating the basic raw material used in the bag, and whether the material is recycled or not. The percentage of recycled material, if used, has to be clearly mentioned, and such bags will be labelled as "not suitable for packaging/storing/carrying food products". The action plan further states that the deadline for drawing up the plans for industries for collection and transportation of used bags for recycling should be ready by October 31, 1998. The

preparation of a status report on plastics waste management with reference to New Delhi, which is being jointly prepared by the Ministry of Environment and Forests and the Central Pollution Control Board, is expected to be ready by September 30, 1998. By the end of November 1998, coordination with concerned departments to restrict the use of polyethylene bags in various public places like parks, zoos, lakes, rivers, etc. is expected to be finalized. It must be appreciated that in spite of much lower levels of per capita consumption of plastics in India, as compared to the economically rich countries, India has realised the importance of plastic waste management quite early, and guideline rules and regulations are in place. Legislations will shortly also be in place.

National as well as international conferences, highlighting the problems and solutions to these global problems have played a key role in bringing the issues on focus. Special mention must be made of the immense contribution of ICS-UNIDO in conducting timely Workshops in economically developing countries of the world, wherein state-of-the-art scientific, technological, economic, and legislation aspects of the field of biodegradable and environmentally acceptable polymers are discussed, and international contacts and established for collaborative projects in the field.

### Solid Waste Management and Recycling in

#### Turkey

Y. KARACA

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Turkey is a large country where lies between Asia and Europe like a bridge. Turkey's population currently stands at 62 million with a growth rate of 1.7% and a young population structure. In addition, in recent years, there has been significant rural-urban migration resulting in rapid population rises particularly within greater municipalities. This rise in the urban population has created significant solid waste management problems for greater areas such as Istanbul, Ankara, Izmir, Diyarbakır, Mersin and Izmit. Waste dumps which are often constructed as hills or on steep slopes are a danger for people living around them.

"The Solid Waste Control Regulation", which became effective on the 14 th of March 1991, aims to control the negative effects on environment being sourced by the huge amount of urban solid waste on the open dumps. This regulation also provides the creation of financial facilities which are needed to serve for the collection, transportation and disposal of solid waste with a certain system in the whole country. Meanwhile, regulation is the legal base for the studies on recollection and evaluation of packaging waste in our country.

### Petkim Petrochemical Co. and Polymer Production in Turkey

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The total plastics consumption in Turkey is realized over one million tones in 1997. The consumption per capita is also realized 17,5 Kg in 1997. About 60% of consumed plastics in Turkey is thermoplastics.

Petkim is the only thermoplastics raw material producer in Turkey. It was founded in 1965. Now it has two petrochemical complex. The first one was into operation in 1971 in Yarımca-İZMİR. According to high domestic demand

the second complex was founded and started-up in 1985 at Aliğa-İZMİR. Petkim is a state company and it is under Government privatization program.

Petkim has been already producing LDPE, HDPE, PVC, PP, PS type thermoplastics raw materials and PTA, PA, ACN, MEG, DEG, PX, OX, caustic, benzene type monomers and intermediates. Major Petkim products are consumed in domestic markets, and rest of them are exported.

### Eureka

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Eureka was launched in July 1985 by seventeen Western European countries and the European Union. Since then it has experienced rapid growth in the number of Research and Development projects, now involving literally thousands of companies, research institutes and universities working in advanced technologies. At the same time, the EUREKA initiative has expanded geographically. Today, the following 25 countries and the European Union are EUREKA Members: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, The Netherlands, Norway, Poland, Portugal, Romania, Russia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom. EUREKA relates primarily following areas of advanced technology: information and telecommunications, robotics, materials, manufacturing, biotechnology, marine technology, lasers, environmental protection and transport technologies. The EUREKA Secretariat in Brussels is the nerve center of the EUREKA network working in close cooperation with the national EUREKA offices and Chairmanship office which is Turkey in this year. EUREKA does not have its own funding. In some countries EUREKA projects have a prefers status, in others there are special EUREKA funds, but in all cases it is the national rules which apply and each project participant simply applies to his/her own national administration in his/her own national language. The overall objective of EUREKA is to raise the productivity and the competitiveness of European industries and economies on the civilian world market. EUREKA supports an ideas about developing a new product, process and service, with market potential. It may also follow an up-stream research and development project, carried out under a national or European Union programme, bringing its results closer to the market-place. EUREKA embrace important advanced technology research and creation of the technical prerequisites for a modern infrastructure and the solution of transboundary problems.

### Biodegradable Polymers as Biomaterials

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Biomaterials are used in prostheses and medical devices for different purposes. Polymers are the most diverse class of the biomaterials. All biomaterials must meet certain criteria and regulatory requirements before they can be qualified for use in medical applications. Biocompatibility is one of the most important requirements. Both nondegradable polymers are designed to degrade *in vivo* in a controlled manner over a predetermined time. The main mechanism of *in vivo* degradation of polymers is 'hydrolytic degradation', in which enzymes may also play a role (i. e. 'enzymatic degradation'). Both natural e.g., collagen, and synthetic e.g., poly( $\alpha$ -hydroxy) acids, biodegradable polymers are used in biomedical applications. Many of the current polymers and processing techniques need to be improved in order to produce polymers with better performance in biological media. An important

trend in related research and development is the synthesis of novel polymers, which would exhibit improved biocompatibility, and be bioresponsive.

### THE EFFECT OF PROCESSING CONDITIONS ON THE STRUCTURAL GRADIENTS DEVELOPED IN INJECTION MOLDED BACTERIAL POLY(3-HYDROXYBUTYRATE-CO3 HYDROXYVALERATE) PARTS

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**ABSTRACT:** The effect of processing conditions on the structure development in bacterial P(3HB-co-3HV) injection molded parts were investigated. The parts were characterized by polarized optical microscopy, Micro WAXS and X-ray pole figure techniques. The preliminary experiments reveal that a distinct structural zones evolve in these parts. They are revealed under crossed polars as zones of distinct interference colors. The coupling of the information from the optical microscopy and X-ray analysis reveal that these spatial variation of color is as a result of spatial variation of chain orientation. The general orientation investigation revealed that the b-crystallographic axes are oriented normal to the molded parts surface and to the flow direction. The effect of processing conditions such as injection speed and the mold temperature as well as copolymer composition will be discussed.

### Absorbable Polymeric Composites as Replacement for Bone Grafts

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Biodegradable polymeric composites have potential applications as temporary fixation materials in the treatment of bone fractures. Among biodegradable composite, self-reinforced poly(L-lactide)'s have been prepared and proposed, due to their high strength, appropriate stiffness and strength retention which can be tailored according to the healing rate of recovering tissues. The key requirement of bone graft dimensional stability over the early stages of bone healing is emphasized so as to provide a stable surface on which osteoblasts and/or their precursor cells may migrate and secrete bone matrix. For this purpose; we were examined the mechanical behaviour of self-reinforced poly(L-lactide) (PLLA, Mv:200.000-500.000) and hydroxyapatite/poly(L-lactide) (HA/PLLA) composites in solution tests. The polymer PLLA, the composites 10wt%, 20wt% and 50wt% HA/PLLA were prepared in rectangular forms. When part of the microstructure of the poly(L-lactide) is transformed into oriented reinforcement elements (like groups of oriented polymer chain forming morphological structures such as microfibrils, fibres, extended-chain crystals etc.) the mechanical strength, modulus and toughness of poly(L-lactide) increase significantly. The combination of a bioactive ceramic (HA) and poly(L-lactide) is expected to result in a promising composite because of its bone-bonding potentials and ability to resorb. A further improvement could be to develop and adapt

surgical techniques more suitable for the use of these implants as well as implant geometries and properties.

### EVOLUTION STRUCTURAL HIERARCHY IN UNI AND BIAXIAL DEFORMATION FIELDS IN POLY LACTIC ACID

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In this presentation, we will discuss our results on the effects of uni and biaxial stretching on the deformation dynamics and film thickness uniformity as well as structure evolved from amorphous precursor PLA films. The use of processing temperatures in the rubbery range between  $T_g+10$  and  $30^\circ\text{C}$  result in varying degrees of crystalline order. Crystalline phase begins to form after substantial deformation has taken place in the films and the level of this tend to be retarded at higher end of the stretching temperatures employed. This was coincident with the retardation of the strain hardening that accompanies strain induced crystallization in these films.

### Production and Characterization of Poly(lactide) Based Biodegradable Nonwoven Matrices

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In this study, we attempted to develop a novel soft tissue filling and/or dressing material. The homopolymer of poly (D,L-lactide) was synthesized by the ring-opening polymerization of D,L-lactide in bulk at  $180^\circ\text{C}$  under nitrogen atmosphere. Stannous octoate was used as the catalyst. The dimer/catalyst ratio was changed for synthesizing polymers with different molecular weights. These polymers were characterized by FTIR, DSC, viscosity and GPC measurements. The PDLA polymers were processed into fibers by two techniques, namely, "wet spinning" and "melt spinning". The PDLA fibers prepared by wet spinning process, were tested for cytotoxicity. Also their *in vitro* and *in vivo* degradations were investigated. In melt spinning process, the polymer was extruded into fiber form by using an extruder and a die. The polymeric matrices were also prepared by using the same technique. Their mechanical properties were investigated. In order to increase the biocompatibility of the PDLA matrices, biological modification was performed by elastin derived proteins (ESP). ESP immobilization was achieved by using a novel technique, the so-called glow-discharge treatment. Two alternative glow-discharge treatment methods were applied to incorporate (immobilize) ESP on the PDLA matrix surfaces. In the first method, the PDLA matrices were treated in an inert gas (i.e., argon) plasma created in the glow-discharge reactor. In the second approach, the PDLA matrices were placed in the glow-discharge reactor, and then treated in an active monomer (i.e., ethylene diamine, EDA) plasma. In this procedure, the PDLA matrices were first treated in the EDA plasma, and then were simply incubated in the glutaraldehyde solution. The glow-discharge treatment power and time were changed in order to see the effects of the treatment conditions on modification. These treated matrices were then immediately immersed in the aqueous solutions containing different amounts of ESP. Maximum ESP immobilizations were achieved in the case of EDA plasma treatment. Following this

information, the elastin adsorption onto the PDLA matrices modified by EDA plasma (carrying also ESP) was also investigated. In order to show the changes on the surfaces, Scanning Electron Micrographs of the PDLA surfaces were taken before and after argon/EDA-glow-discharge treatment and ESP/elastin immobilizations.

### Plastics Production, Import/Export and Consumption and Potential Applications of Biodegradable Polymers in Iran

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There are four major petrochemical complexes in Iran which are located in Abadan, Bandar Imam, Arak and Tabriz. Several monomers and polymers are produced in these complexes. The main products are polyolefines, polyvinyl chloride, polystyrene, styrene-butadiene rubber, the highest consuming plastics domestically and industrially. In Iran plastics solid wastes are mostly used as recycling materials for production of materials as post-consumer recycled goods. There is no biodegradable polymer production in Iran, and although the areas of applications for these materials are obscure and not known at all, but there is a potential social concern for environmental problems which consider plastics wastes as a seriously threatening issue.

### Biodegradable Polymers and Hydroxyapatite Composites

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In this study, two different elastomeric D,L-lactate ve  $\epsilon$ -caprolactone copolymers, namely EV and ET copolymers were synthesized for hard tissue repair. The number and weight average molecular weights and heterogeneity indices obtained by GPC were  $M_n$ :108 000;  $M_w$ :170 000; H.I.:1.56 and  $M_n$ :40 000;  $M_w$ :80 000; H.I.:2.00, respectively. The characteristic peaks of the monomers on the FTIR spectra indicated the formation of the copolymer. <sup>1</sup>H NMR spectra proved the formation of copolymers, and the D,L-lactate/ $\epsilon$ -caprolactone ratios of both copolymers were found as 60/40 from these spectra. DSC thermograms showed that both copolymers (EV and ET) were amorphous and have glass transition temperatures of -22.1°C and -21.2°C, respectively. Hydroxyapatite (HA) with two different size ranges were loaded within both copolymers at three different ratios (20, 40 and 60% in weight). Optical and scanning electron microscope photographs showed that HA particles were homogeneously distributed within the polymer matrices. The polymer-HA composites were easily shaped by hand. Mechanical properties of the composites changed with HA loading, HA particle size, and the molecular weight of the copolymer. Per cent elongation decreased while both yield stress and hardness modules increased with the increase in the HA loading. By using HA with larger particle size, less flexible but stronger composites were obtained. The composites which were prepared with the higher molecular weight copolymer (i.e., EV) were less flexible but stronger. Copolymers were degraded within the Ringer solution in about 6 weeks. The

molecular weight distribution became broader during degradation. Incorporation of HA within the polymeric matrices significantly slowed down the degradation. Much slower degradation rates were observed especially when HA particles with larger sizes were used, and also for the composites with high HA loadings.

### Polymers & Plastics production in Kuwait, Challenges and Opportunites

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The Petrochemical Industry in Kuwait is undergoing major turning point in its history. There are new events that contribute to this episode. The decision of the Kuwait government to privatize the Petrochemical Industry company is one factor, coupled with the reshuffling and merger of the Kuwait Oil Company, the Kuwait National Petroleum Company and the Kuwait Petroleum Corporation. Other related companies have already been privatized in 1996- 1998 period. The other factor is the introduction of new legislation to allow foreign investment in Kuwait. The third factor is the world economic slowdown that was enforced by the collapse of many markets and caused major revision in the chemical industry supply / demand forecast. We will analyze these factors and their effect on the Kuwait Petrochemical Industry with special emphasis on polymers and plastics. We will review the current status of the local industry and provide some insight on future directions.

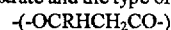
### Synthesis and Applications of Microbial Polymers

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Synthesis common plastics such as polypropylene, polyethylene, polystyrene, polyvinylchloride and polyethyleneterephthalate have been produced hundred million tons each year in order to use mostly packaging materials. Because of their resistant to biodegradation, plastic better and waste proposal increase gradually. There are several limited solutions to cop with the disposal of non degradable plastics: Incineration and recycling of plastic materials have been mentioned as limited solutions.

A partial solution to the increase in plastic litter and the waste disposal problem is the development and the industrial production of degradable materials. The natural polyesters, poly-3-hydroxyalkanoates, PHBs are a class of reserve polyesters produced by a large number of bacteria when subjected metabolic stress in that they are receiving increased attention for possible application as biodegradable, melt processible polymers which can be produced from renewable resources, PHAs have the general repeating units shown below, in which the structure of the R group is dependant upon the carbon substrate and the type of bacteria.



The polymer with R=CH<sub>3</sub>, Poly-3- hydroxybutyrate, PHB, is highly crystalline with a melting temperature of 180 C and a glass temperature of about 5 C polyesters with longer R substituents are also produced by a variety of bacteria,

generally in the form of copolymers which have low degrees of crystallinity and low melting and glass transition temperature values. As a result, these type of PHAs are useful as thermoplastic elastomers, and are also inherently biodegradable.

### **Polymer Production and Solid Waste Management in Azerbaijan**

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The paper describes production of polymers and problems of solid waste management in Azerbaijan. A problem of degradable polymers produced, in particular, carboxy methylcellulose is discussed. Basic data are given on oil refineries and petrochemical production, enterprises processing plastics materials. Characteristic of all major enterprises in these areas is given, nomenclature of their production. Major wastes forming at the enterprises of the area are described and recommendations on their use and disposal.

Problems of waste disposal are discussed from the point of view of environmental control. It has been recommended to establish special co-ordinating body for investigation of current situation with wastes in Azerbaijan and to develop a feasibility study aimed to significant reduction of wastes volumes and their efficient use in the republican economy. Such co-ordination body will allow to discipline and assist the designers, as there still are a lot of cases when design and construction of industrial enterprises take place with undeveloped cycle of processing raw materials and other materials.

### **Environmentally Benign Synthesis of Biocompatible Polyacetylenes**

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China is one of the largest countries in the world to produce polymer resins and to consume plastic products. PVC and PE account for the largest amounts of resins produced and consumed. Meanwhile, China (especially Hong Kong) also imports quite amounts of resins from U.S. and Japan and plastic products from East Asian countries. The increasing use of plastics has caused serious environmental problems, which has already drawn attention of the government and publics. For example, the continuing use of plastic agriculture mulches has deteriorated the soil conditions in many districts of China. In order to solve these problems, degradable plastics (including bio- and photodegradable plastics), especially degradable agriculture mulches are under active development. Degradable plastics have been a very hot topic not only for researchers and administrators, but also for manufacturers, businessmen, investors, and consumers in China including Hong Kong. The research foundations, such as Environment and Conservation Fund and Woo Wheelock Green Fund in Hong Kong, are providing strong financial support to degradable plastics related research projects. Presently, thousands of tons of degradable plastics in film and sheet forms are manufactured and consumed yearly in China. These degradable plastics are produced mainly via the PE/starch and PE/organo-nics biendings. The biodegradable polymer PHB has also been produced via microbial fermentation in a pilot-scale factory for several years in China. The products of PHB are

being explored both for environmental purposes and for biomedical uses. Biomedical products from lactide polymers and copolymers has been on the market for clinical uses developed by China and Hong Kong scientists. We are particularly interested in polymers of acetylenes containing naturally occurring components such as amino acids, glucose, galactose, etc. The purpose of our investigation is to synthesize electrically conducting polymers with biocompatibility. The biocompatible conducting polymers may find potential applications as biomedical materials, e.g. as a material in artificial nerve system. We hope our pioneering exploration will stimulate interest among materials scientists. We have synthesized these polyacetylenes via an environmentally benign approach, i.e. in aqueous but not in toxic organic solutions.

### **Degradable Plastic Films in Agriculture in Taiwan**

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Tainan District Agricultural Improvement Station began in February 1991 to evaluate the feasibility of using degradable plastic films for horticultural crops production. Products from China, Israel, Germany Korea Taiwan and U.S.A were used for comparison. Results are summarized as follow: Macro- and microenvironmental changes in different seasons affected the degradation time of the tested degradable plastic films. The silver/black bio/photo-degradable PE films containing 20% starch from USI Far East Corporation degraded after 56, 83, 38, and 33 days when they were mulched in fall (October, 1991), winter (December, 1991), spring (April, 1992) and summer (August, 1992), respectively. The more the starch were incorporated, the faster the films were degraded. No difference was observed in size, weight, yield, total soluble solids and heavy metal contents of the fruits of cantaloupe and watermelon grown on the beds mulched with various kinds of degradable PE films or traditional PE film. No difference was observed in yield as well as the heavy metal (Fe, Pb, Ni, Cu, Cd and Cr) contents in the edible part of the crops of cabbage mustard and head lettuce that were grown in the soil without or incorporated with debris of degradable PE films in 5 consecutive years. Same results were also obtained in another trial on cantaloupe and paddy rice for 4 consecutive years. Various amounts (0, 4, 8, 16, 32 and 64g) of used degradable PE films were separately mixed with field soil. The mixed soil were used to grow paddy rice in clay pots. No difference was observed in plant height, length and weight of the spike, 1,000-seed weight and the kernel per spike among the treatments at harvesting.

### **Biodegradation of Polycaprolactone and Polycaprolactone - Based Polyurethane in Sea Water**

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The production of basic polymers in Poland and their export and import in last years are presented. There is also same information about the polymer waste in Poland and the effort to solve this problem. Biodegradation is the most desirable long-term future solution for the disposal of the used polymer

materials and require intensive research and development before it becomes practical. It has become a rather widely adopted opinion that biodegradable polymers have a well-grounded role in solving the waste problem. Aliphatic polyesters presently constitute the most attractive class of artificial polymers which can degrade in contact with living organisms. According to literature degradation of aliphatic polyesters in a living environment can result from enzymatic attack or from simple hydrolysis of ester bonds or both. Polycaprolactone is an important member of aliphatic polyester family known as susceptible to biological degradation. The research is carried out on the biodegradability of polycaprolactone and polycaprolactone-based polyurethanes that find extensive industrial applications. Sea water is very interesting as a microbially active environment for degradation of polymers because the fluctuation of water (wind, waves, rain, microorganisms, animals, sunlight, salt in water etc.) all play a part in degradation in nature. The incubation of polymer samples took place in the Baltic Sea water in Gdynia Harbour. There was also a degradation test carried out with PCL and PU in laboratory in liquid medium containing sea water with  $\text{NaN}_3$  to evaluate the resistance of the polymers against hydrolysis. There are presented the characteristic parameters of sea water during the period of investigation. The incubation of polycaprolactone film had been lasted for 6 weeks, but of polyurethane for a period up to 12 months. The weight losses, the tensile strength, morphological changes under optical microscope were tested during the period of biodegradation. Biodegradation of polycaprolactone in a microbially active environment - sea water is very fast. The film is completely assimilated over a period of 6 weeks. This means that polycaprolactone is very sensitive to enzymatic attack of microorganisms in a living environment. The biodegradability of polycaprolactone-based polyurethane is also observed in sea water. After 12 months of incubation time, polyurethanes have lost their mechanical resistance.

### Plastic waste management and the position of EDPs in Slovakia

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Slovakia is a country with rather developed and extensive chemical industry. Chemical industry is the second largest contributor to gross national product (after machine industry) of the country with a 20% share. Production of plastics and plastic products is an important part of it. Several plants are producing plastics, such as polyolefins, PVC, polyamide and several large as well as numerous small companies make products from plastics by extrusion or injection moulding or using other technologies.

In spite of a large portion of plastics consumed, the waste management is on an underdeveloped level. Recycling is the main process in the case of industrial plastics (mixing a small amount of the waste with virgin pellets) which is limited to the producers. The rest is burned or deposited in landfills. Environmentally degradable plastics are not used in Slovakia at all. The item is discussed on a legislative level and few small research teams are active in universities and the Academy of Sciences.

The research on biodegradable plastics is done at the Slovak Technical University (Faculty of Chemistry) on special materials for medical applications based on collagen. In the Slovak Academy of Sciences (Polymer Institute), the blends of polyhydroxy alkanates are investigated intended for various applications, mainly as a packaging material. The topic of biodegradable films aimed at protection of trees and vine grafts is under development. Extensive experiences are in the field of the biomedical materials used for the encapsulation and immunoprotection of living cells. Abovementioned topics will be discussed in relation to the

trends expected in the future and overall public feeling regarding the EDPs.

### Immunoprotection of living cells encapsulated in the polymeric membrane

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A potential treatment for the hormone or protein deficiency states in humans is transplantation of living cells of interest encapsulated in a semipermeable membrane. The premise behind the membrane, based on the biomedical polymeric materials, is to prevent the rejection of cells by their immunoisolation from the host immune system while allowing nutrients to pass freely, hence maintaining the viability and normal functioning of the encapsulated cells. We report on the recently developed microcapsule based on the hydrogel network formed by the polyelectrolyte complexation between the mixture of natural polyanions (sodium cellulose sulfate and sodium alginate) and synthetic polycation (poly(methylene-co-guanidine)) in the presence of sodium and calcium cations. By using this multicomponent recipe, the essential parameters for the capsule design, i.e. capsule mechanical strength, membrane permeability, surface topology, can be highly controlled. We attempted to identify the principles which govern the polyelectrolyte complex formation leading to the capsular semipermeable membrane specifically aimed at the encapsulation and immunoprotection of living cells. The *in vitro* and *in vivo* tests in mice revealed the capsule biocompatibility, non-biodegradability and non-cytotoxicity which are the prerequisite features to be fulfilled for this type of biomedical material. The rat pancreatic cells (islets of Langerhans) enclosed in this capsule and transplanted to different mice models were viable and fully functional as artificial pancreas.

### Starch-Based Biodegradable Materials: Present Situation and Future Perspectives

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Biodegradable polymers constitute a loosely defined family of polymers that are designed to be degraded by living organisms. They offer a possible alternative to traditional non-biodegradable polymers when recycling is unpractical or not economical. The main driving force behind this technology is the solid waste problem, particularly with regard to the decreasing availability of landfills, the litter problem and the pollution of the marine environment by non-biodegradable plastics. Technologies like composting used for the disposal of food and yard waste are the most suitable for the disposal of biodegradable materials together with soiled or food-contaminated paper. Starch-based materials are now industrial products and are leading the still small market of biodegradable products.

The state of art of thermoplastic starch and the results obtained by Novamont on thermoplastic starch complexed with synthetic hydrophilic/hydrophobic copolymers, on thermoplastic starch blended with not compatible synthetic polymers and on thermoplastic starch partially complexed with not compatible or slightly compatible synthetic polymers are revised. As an example of the properties achieved by starch-based materials up to now, the 4 classes of Mater-Bi products currently available on the market are described in terms of processability, physico-chemical and physico-mechanical properties and biodegradation behaviour, in comparison with

polystyrene and low density polyethylene. The results of a Life Cycle Analysis performed by Composto in Switzerland on different alternatives of separate collection of organic waste are also discussed. Starch-based biodegradable materials' future market perspectives are finally presented as a function of the legal environment.