24th International Symposium on Polymer Analysis and Characterization

Book of Abstracts

6-8 June 2011

Conference Centre and Hotel Villa Gualino

Turin, Italy
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Turin, Italy
Locations

Turin was Italy's first national capital. It is a beautiful city, with long colonnaded boulevards, the imposing Piazza Castello, historical cafés and restaurants, and the lively pace of its citizens. The Turin's Royal Residences are listed as "World Heritage Sites" by UNESCO in 1997. Sports cars and chocolate are a matter of pride in the city. It is also home to the Museo Egizio, one of the most impressive collections of Egyptian artifacts in the world. Valentino Park houses an 18th-century castle, botanic garden and medieval village. Turin is only about 2 hours away from Milan, and you can visit Milan before or after the conference.

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The International Symposium on Polymer and Characterization, ISPAC, is a non-profit scientific organization. The purpose of ISPAC is to provide an international forum for the presentation of recent advances in the field of polymer analysis and characterization methodologies. This unique Symposium brings together analytical chemists and polymers scientists involved in the analysis and characterization of polymeric materials. Meeting are held annually, rotating to venues in the USA, Europe and Asia.

**Previous ISPAC Symposia**

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**Future ISPAC Symposia**

2012, The Netherlands
Publication

Papers based on the Invited Lectures, contributed lectures and posters presented at ISPAC-2011 may be submitted for inclusion in a special Symposium issue of the International Journal of Polymer Analysis and Characterization (IJPAC). Contributions, which will receive a peer review, will be accepted by the Editor-in-Chief of IJPAC, Josef Janca (ijpac@ft.utb.cz) exclusively as electronic files, e.g., on a floppy disk, CD, etc., or as an e-mail attachment. The special issue will be published as soon as possible, with a target in late 2011 or early 2012. The Instructions for Authors may be found in issues of IJPAC, or online at the URL: www.taylorandfrancis.com.

Contributions should not exceed 15 pages double-spaced using font Times Roman 12pt, including figures, tables, and references.

The final deadline for manuscript submission (to be considered for this symposium issue) is to be announced.
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Symposium Program
SUNDAY, JUNE 5th

18.00 – 19.00 Registration / Welcome Cocktail

MONDAY, JUNE 6th

8.30 – 9.00 Registration

9.00 – 9.20 G.C. Berry, ISPAC Chair: Symposium Opening

Session 1 POLYMERS FROM RENEWABLE SOURCES

9.20 – 10.00 Invited Lecture
Bioplastics in commodity applications: properties-structure correlation by classical and innovative analytical methods
Mario MALINCONICO, Institute Chemistry and Technology of Polymers–CNR, Naples, Italy

10.00 – 10.40 Invited Lecture
Analytical tools for analyzing long-term properties of renewable polymers and biocomposites
Sigbritt KARLSSON, Royal Institute of Technology, Stockholm, Sweden

10.40 – 11.10 Discussion

11.10 – 11.30 Coffee

Oral Presentations

11.30 – 11.50 NMR and ESR Characterization of Activated Carbons Produced from Pecan Shells
H.N. CHENG, L. H. WARTELLE, K. T. KLASSON, J. C. EDWARDS

11.50 – 12.10 Investigation of the interactions between polysaccharides and multivalent metal ions
A.M. ZELLERMANN, C. MAYER

12.10 – 12.30 Experimental characterization of liposomes stabilized by polyelectrolytes and mechanism of interaction involved
M.RINAUDO, F.QUEMENEUR, B.PEPIN-DONAT

12.45 – 14.00 Lunch
Session 2  **ASSESSING POLYMER STABILITY**

14.00 – 14.40 Invited Lecture
*Assessing oxidative degradation in polymers: Chemiluminescence and other methods*
**Norman BILLINGHAM**, University of Sussex, UK

14.40 – 15.20 Invited Lecture
*Photo-induced chemiluminescence as a sensitive probe for polymer photodegradation*
**Keith MILLINGTON**, CSIRO Materials Science and Engineering, Belmont, Australia

15.20 – 15.50 Discussion

15.50 – 16.10 Coffee & Tea

**Oral presentations**

16.10 – 16.30 *Contribution to the degradation of some biopolymers: improvement of their thermo and thermo-oxidative stability by natural antioxidants*
**L. RYCHLÁ, A. EBRINGEROVÁ, I. SROKOVÁ, K. CSOMOROVÁ, J. RYCHLÝ**

16.30 – 16.50 *Characterization of degraded paper in the field of cultural heritage*
**A.L. DUPONT**

16.50 – 17.10 *Evaluation of curing behavior of epoxy resins by MALDI-mass spectrometry combined with supercritical methanalysis*
**H. OHTANI, M. HANAOKA, M. MATSUURA**

17.10 – 17.30 *Assessment of degradation of polyurethanes, nitrocellulose and acetate of cellulose as the least stable polymers in museum artifacts*
**J. RYCHLÝ, A. LATTUATI-DERIEUX, L. MATISOVÁ-RYCHLÁ**

17.30 – 17.50 *Evaluation of the decay degree of Tilia cordata wood by different analytical methods*
**C.M. POPESCU, M.C. POPESCU, G. LISA, B. C. SIMIONESCU**

18.00 – 20.00 **Wine & Cheese@Poster Session**
TUESDAY, JUNE 7th

Session 3  
**MOLECULAR AND STRUCTURAL CHARACTERIZATION**

9.00 – 9.40  **Invited Lecture**  
*Recent developments and advances in polyolefin characterization*  
Benjamin MONRABAL, Polymer Characterization, Valencia, Spain

9.40 – 10.20  **Invited Lecture**  
*2D-LC characterization of branched polymers*  
Taihyun CHANG, Pohang Univ, Rep. Korea

10.20 – 10.50 Discussion

10.50 – 11.10  **Coffee**

**Oral presentations**

11.10 – 11.30  **Statistical two-dimensional NMR: Assignment of complicated resonances due to the carbonyl carbons of methacrylate copolymers**  
T. HIRANO; H. MOMOSE; T. MAEDA; T. NAONO; S. ASAKAWA; Y. KATSUMOTO; K. UTE

11.30 – 11.50  **Characterization of UV curable multimodal oligomers using a semipreparative GPC method combined with a triple detection system**  
M. SCOPONI; S. ROSSETTI

11.50 – 12.10  **Advanced Structural Characterization of Polyolefins – Branching using High Temperature Triple Detection GPC**  
J. SANCHEZ, B. SABAGH, W. S. WONG, P. CLARKE

12.10 – 12.30  **Pitfalls in the Interpretation of the Results of SEC Measurements**  
P. KRATOCHVÍL, M. NETOPILÍK

12.30 – 12.50  **Tensile Modulus, Poisson Ratio, Storage Modulus, Indentation Modulus and PALS analysis of Polypropylene/Cycloolefin Copolymer Blends**  
L. FAMBRI, G. ZAMFIROVA, N. DJOURELOV, D. LORENZI, V. GAYDAROV, S. PENEVA

12.50 – 13.10  **Online Monitoring of Acrylic Acid Polymerization Reactions**  
P. CHEN, N. LORBER, A. BOYER, J. WILSON, E. MIGNARD

13.15 – 14.30  **Lunch**
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14.30 – 15.10 Invited Lecture
From new materials to a complete device: the role of characterization techniques in the development of novel polymer solar cells
Chiara CARBONERA, Solar Energy Res Center for Non-Conventional Energies – Eni, Italy

15.10 - 16.00 Invited Lecture
Controlled crystallization in semiconducting polymer thin films
Sabine LUDWIGS, University of Stuttgart, Germany

16.00 – 16.30 Discussion

16.30 – 16.50 Coffee & Tea

Oral presentations

16.50 – 17.10 Biodegradability of Plastics: Standards and Certifications
F. DEGLI INNOCENTI

17.10 – 17.30 Nanoporous Crystalline Polymers and Energy Applications
C. DANIEL, J. VITILLO, G. SPOTO, G. GUERRA

17.30 – 17.50 Hyphenated DSC and Raman to provide deep insight in polymer structure
M. COLETTI, C. GRACIA, P. CRESPI

18.00 – 19.30 Posters

20.00 Symposium dinner

WEDNESDAY, JUNE 8th

Session 5  CHARACTERIZATION OF MESO AND NANO STRUCTURES

9.00 – 9.40 Invited Lecture
Studies of nanostructured diblock copolymer systems using small-angle scattering in transmission and grazing incidence geometry
Dorthe POSSELT, University of Roskilde, Denmark
9.40 – 10.20 Invited Lecture

Block copolymer vesicles as chemical nanoreactors and molecular release systems: the characterization challenge

G. Julius VANCZO, University of Twente, The Netherlands

10.20 – 10.50 Discussion

10.50 – 11.10 Coffee

Oral presentations

11.10 – 11.30 TD-NMR investigation of nanoconfined soft phases in SEBS
R. SIMONUTTI; L. MAURI; M. MAURI

11.30 – 11.50 Analysis of Multi-Component Polymer Blends with the Confocal Raman AFM
K. WEISHAUP; U. SCHMIDT, T. DIEING, W. IBACH, and O. HOLLRICHER;

11.50 – 12.10 FTIR Step Scan Photoacoustic Spectroscopy applied to the study of micro and nanostructures in Fluorinated Polymers
S. RADICE

12.10 – 12.30 Nanoscale Chemical Spectroscopy with the Atomic Force Microscope
J. SCHLUETTER, C.B. PRATER, D. COOK, R. SHETTY, K. KJOLLER

12.30 – 12.50 Microindentation Study on Polypropylene/Cycloolefin Copolymer Blends
G. ZAMFIROVA, V. GAYDAROV, D. LORENZI, L. FAMBRI

13.00 End of Symposium and announcement of 2012 edition

13.00 – 14.00 Lunch

14.30 Excursion departure from Villa Gualino
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**POLYMERS FROM RENEWABLE SOURCES**

**IL1.** Bioplastics in commodity applications: properties-structure correlation by classical and innovative analytical methods  
**Mario MALINCONICO;** Institute Chemistry and Technology of Polymers–CNR, Naples, Italy

**IL2.** Analytical tools for analyzing long-term properties of renewable polymers and biocomposites  
**Sigbritt KARLSSON;** Royal Institute of Technology, Stockholm, Sweden

**OP1.** NMR and ESR Characterization of Activated Carbons Produced from Pecan Shells  
**H.N. CHENG, L. H. WARTELLE, K. T. KLASSON, J. C. EDWARDS;** USDA Southern Regional Research Center, USA

**OP2.** Investigation of the interactions between polysaccharides and multivalent metal ions  
**A.M. ZELLERMANN, C. MAYER;** University Duisburg-Essen, Germany

**OP3.** Experimental characterization of liposomes stabilized by polyelectrolytes and mechanism of interaction involved  
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**ASSESSING POLYMER STABILITY**

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**IL4.** Photo-induced chemiluminescence as a sensitive probe for polymer photodegradation  
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**OP4.** Contribution to the degradation of some biopolymers: improvement of their thermo and thermo-oxidative stability by natural antioxidants  
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A.L. Dupont; Muséum national d’Histoire naturelle, France

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“Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Romania

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P. KRATOCHVÍL, M.NETOPILÍK; Institute of Macromolecular Chemistry, Czech Republic
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IL8. Controlled crystallization in semiconducting polymer thin films  
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OP15. Biodegradability of Plastics: Standards and Certifications  
F. DEGLI INNOCENTI; NOVAMONT, Italy

OP16. Nanoporous Crystalline Polymers and Energy Applications  
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OP17. Hyphenated DSC and Raman to provide deep insight in polymer structure  
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OP19.  *Analysis of Multi-Component Polymer Blends with the Confocal Raman AFM*
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OP20.  *FTIR Step Scan Photoacoustic Spectroscopy applied to the study of micro and nanostructures in Fluorinated Polymers*
  S. RADICE; Solvay Solexix, Italy

OP21.  *Nanoscale Chemical Spectroscopy with the Atomic Force Microscope*
  J. SCHLUETTER, C. B. PRATER, D. COOK, R. SHETTY, K. KJOLLER; LOT Oriel GmbH & Co., Germany

OP22.  *Microindentation Study on Polypropylene/Cycloolefin Copolymer Blends*
  G. ZAMFIROVA, V. GAYDAROV, D. LORENZI, L. FAMBRI; Transport University “T.Kableshkov”, Bulgaria
Bioplastics in Commodity Applications: Properties-Structure Correlation by Classical and Innovative Analytical Methods

Mario MALINCONICO*

Institute on Polymer Chemistry and Technology, CNR, Pozzuoli, Italy

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Bioplastics are made of biodegradable polymers, often natural in their origin and always able to be recognized by micro-organisms which use them as substrate for their growth. In order to transform biodegradable polymers into a bioplastics, it is necessary to perform physical as well as chemical-physical treatments and to blend them with additives which must also be “sustainable” and “biodegradable”. The lecture reviews several experiences on the processing of synthetic and natural biodegradable polymers and on their formulation with additives coming from natural sources to obtain blends, composites or gels. The families of investigated bioplastics are hereafter described:

Mater Bi with natural additives

A polyphenol-containing extract from winery bio-waste (EP) has been used as an additive for a starch based polymer (Mater-Bi). EP was used to tailor Mater-Bi properties, thus avoiding the use of synthetic polymer additives. It was found that EP was able to efficiently modulate the processing, mechanical, thermal and biodegradation properties. The observed decrease in melt viscosity showed that EP could improve productivity in polymer processing. Owing to the plasticizing activity of the additive, larger values of elongation at break were found. Finally, the bio-disintegration rate of doped Mater-Bi decreased, thus suggesting that EP acted as an antimicrobial agent by interfering with the bio-digestion of the polymer films.

Poly(hydroxy butyrate) with natural additives

Poly(3-hydroxy butyrate)(PHB) is a bacterial polyester widely investigated in the last 2 decades for its biodegradability and biocompatibility. Due to its high crystallinity and to an unstable melt behaviour, its exploitation has been severely limited. With the aim to improve mechanical and processing behaviour, PHB has been processed in the presence of winery
biowastes (EP). It has been observed that, increasing the EP content, PHB improves its thermal resistance and, consequently, melt processing can be carried out in more safe conditions.

**Polylactic acid for packaging**

PLLA films containing different amounts of α' and α crystal forms were prepared by annealing quenched PLLA at different temperatures. The polymorphic structure of the films was analyzed by X-ray diffraction. Mechanical properties and permeability to water vapor were investigated as a function of degree of crystallinity (\(w_C\)) and related to crystal polymorphism developed during annealing. The polymorphic structure of PLLA significantly affects mechanical and barrier properties.

**Polysaccharides in gel and spray formulations**

Mulching with plastic films is a practice that has improved very much, in the last decades, crop production saving at same time water and reducing chemical. Unfortunately, most of the used plastic films are buried in soil or burnt in open air, with strong impact on the environment. A sustainable approach has been developed, in which a waterborne solution of natural polymers (polysaccharides of marine and terrestrial origin) and cellulose fibers is prepared and sprayed on an agricultural soil to form a film resistant for the time required for the mulching application, and then biodegraded in soil by microflora. Also, biodegradable nursery pots can be obtained by thermoforming or wet forming technologies, which are then left in the soil, with reduced stress for the plants and positive effects on the soils structure.

Polysaccharide gels and films are also proposed for the preservation of fresh dairy products and as smart packaging for the controlled de-hydration of fruits with preservation of their sensorial characteristics, when compared to industrial de-hydration processes.
Analytical Tools for Analyzing Long-Term Properties of Renewable Polymers and Biocomposites

KARLSSON, SIGBRITT*

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Presently, on leave to act as Vice-Chancellor of Skövde University, SE-541 28 SKÖVDE,

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The concept of sustainability within polymeric materials usually implies that renewable resources are used to manufacture products. Combinations of renewable polymers such as starch, polylactides (PLA) in combination with biofibres (e.g. cellulose from wood, agricultural waste) are promising materials that are already in use in vehicles, packaging etc. Renewable and biopolymers usually have a more complicated chemical structure which put new demands on the analytical techniques. To reach sustainability this in turn put demand on a careful selection of renewable resources together with the manufacturing of low emitting polymeric materials to lessen the environmental impact. A combination of traditional, renewable and recycled resources will gradually be combined in new polymeric materials and biocomposites.

The objective of this presentation is to review various analytical tools for analyzing the long-term properties of renewable polymers and biocomposites. Gradual changes in the polymeric properties are observed during long-term use. Analytical tools to monitor long-term properties range from methods that detect macroscopic to microscopic properties and also changes at the chemical structure level (1-5). A series of extraction methods is needed to monitor the formation of low molecular weight compounds from the polymer, residues from the polymerization and additives [6][7]. A more detailed picture is obtained by the use of MALDI-MS where molar mass changes are obtained simultaneously with structure fragments [9-10].

Long-term properties may be modeled in order to explain changes in real-life samples, this was explored in a work involving silk, where a conservation method was to be developed for a rare artefact [11]. New insights in the long-term properties of renewable polymers and...
biocomposites were found using MALDI-MS [12-13]. The presentation will cover a set of analytical tools which were used to monitor simulated long-term use of polymers and biocomposites. In addition, a selection of results of aged renewable polymers and biocomposites are presented demonstrating the comparison to real-life long-term property changes.

References

NMR and ESR Characterization of Activated Carbons Produced from Pecan Shells

H.N. CHENG, LYNGDA H. WARTELLE, K. THOMAS KLASSON

Southern Regional Research Center, USDA Agricultural Research Service, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA

John C. EDWARDS

Process NMR Associates, LLC, 87A Sand Pit Road, Danbury, CT 06810, USA

A large number of solid-state NMR and ESR experiments were explored as potential tools to study chemical structure, mobility, and pore volume of activated carbon. We used a model system where pecan shells were activated with phosphoric acid, and carbonized at 450°C for 4 h with varying amounts of air flow. Through the use of different NMR experiments (e.g., CP-MAS, SPE-MAS, and DD-MAS) several structural parameters were calculated such as mole fraction of bridgehead aromatic carbons, number of carbons per aromatic ring system, and number of phenolic carbons per aromatic ring system. The relaxation time measurements (T₁, TCH, and T₁ρ) were indicative of the relative mobility of different structural units. ESR spectra showed the presence of p-type aromatic free radicals in the carbonized samples with a slight shift in g value with increasing oxidation. The combined NMR and ESR data give a consistent picture of the carbon structure and the carbonization process, which is not easily available otherwise. In addition, the ¹H NMR data on adsorbed water are shown to be consistent with the trends in the amount of pore volumes for different samples of activated carbons.
Investigation of the Interactions Between Polysaccharides and Multivalent Metal Ions

ZELLERMANN, A.-M.*; MAYER, C.

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The removal of heavy metal ions and other toxic substances classified as waterhazards, is a major aspect of water treatment worldwide.

Because of the risks to mankind and the environment which can be correlated with the presence of such materials, the need for the discovery of an effective cleaning possibility becomes of great interest in science and research. As a result, the sources of these pollutants and the resulting consequences are versatile and far-reaching.

In addition to industrial wastewaters, which often include high concentrations of various heavy metals and are thus often dangerous to the environment if not handled appropriately, accidents and natural disasters may also cause contamination of groundwater, rivers, lakes and oceans (e.g. red sludge, Hungary).

In this context, the increased content of zinc, arsenic, copper, cobalt, cadmium and uranium in the ground and surface water in the areas surrounding the copper and gold mines of South Africa can be mentioned as well.

But such contaminations are not always the result of human actions. The great amount of arsenic in the waters of Bangladesh is just one example of a problem whose origin lies in nature.

All of these aspects show how important the development of a simple, effective, inexpensive and non-polluting method for metal removal in water and sewage treatment is.

In this case, an already existing, naturally occurring possibility for removing harmful substances is desired, ideally one, which is also flexible enough to be adjusted to each kind and amount of pollution.

One such option may exist in the use of polysaccharides, which form the main components of the
extracellular, polymeric substances (EPS) of microorganisms in biofilms.

The mostly anionic polymers such as hyaluronate, xanthan and alginate show the ability to bind multivalent metal ions such as lead, cadmium or copper ions, and as a result detract these harmful substances from the surrounding system.

The use of biofilms is connected with the advantage that these films have a certain resistance and surface adhesion which allows applications even in the most extreme situations, such as in reactors with strong flows or harsh conditions.

The increasingly significant interest related to the interactions between polysaccharides and different multivalent ions can be investigated using pulsed field gradient nuclear magnetic resonance spectroscopy (PFG-NMR) or atomic force microscopy (AFM).

Whereas uncharged polysaccharides do not develop interactions, anionic representatives show changes in their structure and behaviour which are correlated to the concentration of the multivalent ions and result in changes of the diffusion properties of the polymer chains in water.

The charged polymer chains which, due to repulsive forces originally form nearly elongated chains, bind the metal ions, resulting in increased entanglement. Further addition of metals eventually leads to an aggregation of several polymer chains.

It is possible that these effects may influence the structure and characteristics of the entire biofilm embedding the polysaccharides. This can also change its surface adhesion properties, resulting in lowering or even supporting their application in water treatment.

References


Experimental Characterization of Liposomes Stabilized by Polyelectrolytes and Mechanism of Interaction Involved

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Depending on their size, liposomes are commonly used as template to develop, either efficient drug carriers with Large Unilamellar Vesicles (LUV, 100 nm < diameter < 500 nm) or pertinent cell mechanical models with Giant Unilamellar Vesicles (GUV, 0.5 µm < diameter < 100 µm). In the present work, we focus on the modification of the structural and consequently mechanical properties of zwitterionic DOPC lipid membranes by coating with two biocompatible charged polysaccharides (cationic chitosan at pH < 6.5 and anionic hyaluronan at pH > 2.0).

Firstly, using a series of complementary techniques on LUVs and GUVs, we show that polyelectrolytes are adsorbed on DOPC vesicles whatever their relative charge signs (tunable by pH), reveal the electrostatic origin of the interaction between polyelectrolytes and zwitterionic lipidic membranes, show the role of their respective charge densities on the amount of adsorbed polymer and evidenced that the polymer chemical structure controls the adsorbed chain conformation at the vesicle surface: chitosan adsorbs flat while hyaluronan forms loops and trains. We also observe that addition of oppositely charged polyelectrolyte causes a reverse of the net charge of the complex lipidic system and the formation of a finite vesicles aggregate when its net charge becomes equal to zero (isoelectric point); further polyelectrolyte addition, leads to separation of the aggregated vesicles and formation of overcharged isolated stable coated vesicles. These isolated coated liposomes obtained in excess of polyelectrolyte exhibit an enhanced resistance against osmotic, pH or salt shocks if compared to bare vesicles. We interpret these results within the frame of a patch-like structure of the polyelectrolyte coated membranes, consisting in the alternation of bare and polymer coated domains.

Secondly, we have demonstrated that the coated membrane structure highly affects the value of the mechanical parameters obtained by compression between two planes (Atomic Force Microscopy) or point-acting force (by hydrodynamic membrane tether extrusion). With AFM, we have demonstrated from original and reproducible compression experiments on chitosan-coated GUVs that
polyelectrolyte coating increases the stretching moduli of the lipid membranes. From membrane nanotubes extrusion experiments, we have demonstrated that coating induces a spontaneous curvature responsible for spontaneous ejection of nanotubes from coated vesicles under osmotic deflation.

Further study will be developed to produce multilayered coated vesicles with controlled ionic charge to be adapted with different application constraints.

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Oxidative degradation is the Achilles’ heel of most synthetic polymers and monitoring oxidation is important both in the practical use of polymers and in the laboratory testing of antioxidant formulations. It is also very important for the understanding of synergism between oxidation and biodegradation, and for assessing the recyclability of polymers. For these reasons there is major interest in methods of assessing oxidation.

The problem of assessing degradation and trying to understand the chemistry involved is that polymers are rather intolerant of chain scission by degradation and often lose their mechanical properties at very low levels of chemical modification. At the same time the products of oxidation can be complex and are bound to the polymer, so that conventional separation and analytical methods are of limited value.

This presentation will review two approaches which have proved useful in studying degradation.

The use of IR spectroscopy in degradation studies is well established. However, two advances have increased the power of IR dramatically. The first in the development of the FTIR microscope, which allows profiling of oxidation. The second is the development of gas-phase derivatisation reactions which convert specific functional groups in the polymer into new groups with stronger and better resolved absorption bands.

A more recent development is the use of single photon counters to detect the low levels of light (chemiluminescence, CL) emitted by oxidising polymers. CL analysis in oxidising atmospheres, gives information on induction time and rate of oxidation, whilst the emission accompanying heating in inert atmosphere correlates with peroxide content in oxidised materials. CL provides an ultra-sensitive way of detecting oxidation but is limited by difficulties of quantitative analysis and by uncertainties about the emission mechanism in particular circumstances.

Coupling a CL detector to a scanning calorimeter allows simultaneous CL/DSC data to be obtained. This has advantages for measuring oxidation induction times as the CL detector is very sensitive to oxidation but does not sense phase changes or other thermal events in the sample. A CL instrument has been built around a high pressure cell, which allows operation at up to 25 bar. This makes it
possible to use lower temperatures and higher oxygen pressures as improved ways of accelerating degradation without changing sample morphology, antioxidant solubility or sample volatility.

Although modern photomultiplier tubes are sensitive and reliable CL detectors, they are mechanically delicate and easily damaged by exposure to light. In recent years charge coupled device (CCD) cameras have become sensitive enough to detect CL emission from polymers. Coupling a CCD camera to a precisely controlled hot stage allows oxidation of as many as 6 - 10 samples to be studied at once. Correlation with oven ageing is excellent and the new approach allows considerable savings of time.
Photo-induced Chemiluminescence as an Early Indicator of Polymer Degradation

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Sunlight exposure is a key causative factor in the degradation of polymers. Assessing the performance of engineering polymers and high-quality coatings always involves prolonged exposure times, often between $10^2$ and $10^4$ hours in an accelerated weathering environment [1] or over four years of outdoor weathering [2], leading to loss of mechanical properties, embrittlement, yellowing, loss of gloss and surface fracturing or chalking.

There is a clear need for new techniques that can predict the weathering performance of polymers and organic materials at an early stage well before degradation becomes apparent. It is well known that UV degradation occurs via a free radical chain reaction known as autoxidation, where atmospheric oxygen rapidly scavenges free radicals in the polymer forming macroperoxy radicals and hydroperoxides. If the number of free radicals formed during the early stages of oxidation could be quantified, it may be possible to predict the weathering performance. Moreover one could then measure the effects of polymer additives such as antioxidants, light stabilisers and UV absorbers on the free radical population. This would be of great assistance in optimising an appropriate additive formulation.

The standard laboratory method for studying organic free radicals is electron spin resonance (ESR). One of the constraints for using ESR is that most polymers of interest have a glass transition close to room temperature and free radicals therefore have very short lifetimes due to their high mobility. Nevertheless two techniques for applying ESR to study polymer weathering have been described. Gerlock [3] doped polymer films with a nitroxide spin trap which resulted in formation of more stable, long-lived radicals when the film was exposed to UV light. By varying the concentration of nitroxide in the film, the photoinitiation rate for undoped polymer was obtained via extrapolation. Other groups have described low-temperature ESR methods, increasing the radical lifetimes by working at 140K [2] and 120K [4].

A far simpler way of quantifying the number of free radicals in organic materials is by measuring chemiluminescence (CL) emission. Most polymers emit CL when they undergo oxidative degradation which originates from the bimolecular reaction of macroperoxy radicals, creating an excited carbonyl. The reaction has a very low quantum yield ($10^{-8} – 10^{-5}$) but highly sensitive photon counters make CL detection from most polymers straightforward. CL is already used extensively to study the thermal degradation of polymers, but photo-induced chemiluminescence (PICL) has been largely neglected. We carried out a reversible
modification to a commercial Lumipol 3 thermal CL instrument to allow samples to be irradiated within the sample cavity using selected wavelengths from a medium-pressure mercury arc by means of a liquid light pipe attached to a special adaptor [5]. In order to separate the PICL signal from photophysical light-emitting processes including phosphorescence, a strict experimental protocol is used as previously described by George et al [6]. An example of the observed PICL decay profiles from cast ethyl cellulose films is shown in the Figure below. Doping the film with a photoinitiator (Irgacure 2959) or UV absorber (Tinuvin 400) increases or decreases the intensity of PICL emission, as expected.

We have reported PICL studies on fibrous polymers and proteins [5], determined the photostability of wool keratin doped with photocatalytic TiO2 [7] and studied the effect of dyes on PICL emission [8]. We have shown that PICL decay profiles do not follow first or second order kinetics but can be modelled using second order kinetics by assuming that an unreactive fraction of macroperoxy radicals is present in the heterogeneous polymer [9].

References

Contribution to the degradation of some biopolymers: improvement of their thermo and thermo-oxidative stability by natural antioxidants

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One of the possible routes how to reduce worldwide increasing plastic wastes from crude oil-based materials is their replacement – at least partially - by biopolymers obtained from renewable resources. All components (additives, inhibitors, etc.) of fully biodegradable materials have to be bio-compatible, as well. Natural antioxidants extracted from different plants, herbs and spices represent an alternative to the synthetic antioxidants. They are considered for stabilization of synthetic polymers as they are biologically degradable in nature. This is also the reason why they may be of interest in food industry and in medical packaging\textsuperscript{1}. One of the first natural antioxidants used was \textit{α}-tocopherol in LDPE\textsuperscript{2}.

In recent years, modified polysaccharides have attracted the research interest as promising materials with a wide range of applications for food and pharmaceutical industries, cosmetics and biotechnology. There is a considerable interest in increasing the utilisation of crop residues such as cereal straw, corn hulls, corn cobs, etc. Xylans comprise roughly 37% of corn cobs and represent biopolymers for direct applications as well as a raw material for the production of new polysaccharide derivatives\textsuperscript{3}.

In this paper we have estimated the stabilizing efficiency of natural biopolymers such as glucuronoxylan (GX) and carboxymethyl cellulose (CMC with degree of substitution DS=0.5) chemically modified by cinnamic acid (GX-CA9 and/or additivated with ferulic acid and antioxidants).

Cinnamic acid itself has the protective effect against oxidation, however, its volatility is rather high at the temperatures of polymer’s processing. To avoid this problem xylan was modified by esterification with cinnamoyl chloride under homogeneous reaction conditions.

\[
\text{Xylan-OH} + \text{CH}_2\text{C} = \text{CH} + \text{HCl} \xrightarrow{\text{DMF, Pyr}} \text{Xylan-O-C-CH}_2\text{C} = \text{CH} + \text{HCl}
\]

Maximum degree of substitution (DS) was 0.55.
Antioxidative efficiency of acids was evaluated by chemiluminescence measuring number of emitted counts during degradation of sample pure and/or stabilized in nitrogen and oxygen atmosphere. These measurements were compared and proved by thermogravimetry.

Fig. 1. The dependence of $I_{CL}$ and TG on temperature $T$ in $O_2$ for GX pure (1) and for GX-AC (2- DS=0.03) and (DS=0.55) (constant $v_{heating} = 5^\circ C/min$).

Fig.2. Chemiluminescence isotherms (T=170 °C) during ageing of GX pure and GX-AC in oxygen atmosphere.

Fig. 1. and 2 show, that xylan with cinnamic acid esterified to the polymer chains decreases the intensity of chemiluminescence and shifts the curve to the higher temperatures (Fig.1) and/or time in either nonisothermal or isothermal mode (Fig.2). The chemiluminescence intensity ($I_{CL}$) decreases with DS of stabilized samples when compared with pure xylan. The same is valid for CMC pure and with esterified CA.

References

Characterization of Degraded Paper in the Field of Cultural Heritage

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Understanding the parameters influencing the durability of historic papers and lignocellulosic materials in general is a fundamental area of research in the field of preservation of historic paper-based artefacts. The state of degradation of cellulose determines the mechanical properties of paper, which ultimately is the criterion to be related to the useful lifespan of paper. The main cause of decay of paper is its acid content in combination with time and conditions of exposure, as upon ageing cellulose undergoes acid catalysed hydrolysis and oxidation reactions. The macromolecular characterisation of cellulose is thus a pivotal aspect in the research. Sensitive analytical methods have to be developed to possibly enable diagnostics of the alteration levels with application to historic objects. In that respect, size-exclusion chromatography (SEC) is a technique of choice because it is very sensitive and appropriate to evidence early degradation. Coupled on-line with multi-angle light scattering (MALS) detection, the information on the molar mass distribution and the polydispersity of a polymer is extremely precise as absolute values of the molar mass averages ($M_n$, $M_w$, $M_z$) are determined as well as size distribution with parameters such as the root mean square radius (rms). The great advantage of online MALS experiments is that calibration is not required, which is important in the case of cellulose, as standards are not commercially available. A refractometer (DRI) is needed to measure the concentration of the solute in each slice of the chromatogram, for which the polymer is considered monodisperse, and to compute molecular weight. SEC/MALS-DRI thus provides a fine and precise characterisation of cellulose upon dissolution of paper in an appropriate solvent ($N,N$-Dimethylacetamide with lithium chloride).

Another aspect to be considered for the comprehensive study of the deterioration of cellulosic cultural heritage relates to the by-products from paper degradation. A large part of the molecules formed have low-molar mass, and depending on which polymer in the paper they originate from (cellulose, hemicelluloses, lignin), they are aliphatic and aromatic compounds with carbonyl, and carboxyl functionalities, and carbohydrates. Due to sampling constraints, a primary aim in the field of cultural heritage preservation science is to establish useful micro-destructive, and whenever possible non-invasive, methodologies. As material sampling is often unavoidable, these techniques should evolve towards sample miniaturisation and reduced solvent consumption. Capillary electrophoresis (CE) uses
aqueous buffers and is well adapted to minute amounts of sample. The performance of this technique in terms of selectivity, efficiency and resolving power is even enhanced when coupled to high sensitivity detectors such as mass spectrometers (MS), which provide molar mass (m/z) and some structural information. CE/ESI-MS (electrospray ion source) in particular is especially adapted for the analysis of complex samples.

In this lecture, some applications of the use of SEC/MALS-DRI, CE/UV and CE/ESI-MS for the characterisation of paper degradation in the field of conservation science will be given. These include the study of the impact of gelatine sizing in paper during ageing [1,2], the degradation occurring at the wet/dry interface resulting in tideline formation [3], and the characterisation of historic samples and artificially aged papers of diverse origin.

References


Evaluation of Curing Behavior of Epoxy Resins by MALDI-Mass Spectrometry Combined with Supercritical Methanolysis

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Structural characterization of the cross-linking networks in cured resins has been not an easy task even using advanced spectroscopic methods mainly because of their insoluble nature. Recently, the authors reported a technique to analyze the chain length distribution of network junctions in photocured acrylic resins using matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) combined with supercritical methanolysis of the resin samples\(^1\),\(^2\). In this work, the curing behaviors of thermosetting epoxy resins were evaluated by this technique.

The bisphenol-A diglycidyl ether type epoxy prepolymer (average degrees of polymerization; \(n = 4.44\)) was mixed with hexahydrophthalic anhydride (hardener) and benzyl dimethyl amine (curing catalyst) in weight ratio 85.3:14.2:0.5 and then thermally cured in a gas chromatograph (GC) oven set at 120°C for up to 2 hours. The cured resin sample was freezer-milled, and the aliquot (2 mg) was sealed into a stainless steel tube (1/4 inch o.d., 7 cm long) with dehydrated methanol (0.7 ml). The resin in the tube was subjected to supercritical methanolysis at 270°C for 2 hours in the GC oven. The methanolysis product was measured by MALDI-MS using dithranol as a matrix reagent and NaI as a cationization reagent.

Fig. 1 shows typical MALDI mass spectra of methanolysis products of (a) uncured prepolymer, (b) intermediate cured resin for 20 min, and (c) completely cured one for 2 hours. Based on the observed m/z values, the main products for the uncured prepolymer (□) were identified to the components with methoxy groups at both chain ends, while those for the completely cured resin (□) were to those end capped with two hydroxyl terminals. Moreover, in the spectrum for the intermediate cured resin, the products with a methoxy and a hydroxyl group at each terminal (♦) were also observed. As shown in Fig. 2, this result demonstrates that the unreacted epoxy group should decomposed into a methoxy and a hydroxyl groups by methanolysis whereas the ester linkages formed between the prepolymer and the anhydride be hydrolyzed into hydroxyl groups at the chain end of the prepolymer moiety. The relative peak intensities among the observed methanolysis products, therefore, the curing behaviour of the epoxy resin samples can be discussed in detail.
Fig. 1 MALDI mass spectra of methanolysis products of (a) uncured prepolymer, (b) intermediate cured resin for 20 min, (c) completely cured resin for 2 hours.

Fig. 2 Methanolysis reactions at uncured epoxy groups and ester linkages in cured resin.

References


Assessment of Degradation of Polyurethanes, Nitrocellulose and Acetate of Cellulose as the Least Stable Polymers in Museum Artifacts

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From the set of plastics appearing in museums collections there are some having the potential for causing damage to other museum’s objects, notably metals. Of them the degradation of nitrocellulose, acetate of cellulose, plasticized polyvinylchloride, fully vulcanized hard rubber (ebonite and vulcanite) and polyurethanes and evaluation of the remaining service life should be examined with the highest priority.

In the present paper, degradation of nitrocellulose, acetate cellulose and polyurethanes (ether and ester) was assessed. The polymers were aged artificially and the progress of the degradation was evaluated by testing these polymers by DSC, thermogravimetry, chemiluminescence and ATR FTIR spectroscopy. An example of the chemiluminescence response on various routes of ageing of polyurethane foams is given in the Fig. 1.

Fig. 1. The chemiluminescence runs on polyester urethane (a) and polyether urethane (b) foams aged at relative humidity 50%. 1a and 1b are reference samples, 2a aged at 90°C for 252 days, 2b aged at 90°C for 56 days, 3a and 3b aged by light at 25°C both for 15 days.
Polyether urethane foam was composed from polyether (polypropylene glycol based) polyol part and toluenediisocyanate part. Polyester urethane foam was composed from polyester (adipic acid based) polyol part and toluenediisocyanate (TDI) part. Both polyurethanes were supplied by RAJA company, Paris.

Faster oxidation of polyether urethanes aged by heat at the medium range of temperatures (120-180 °C) – 2b which is due to hydroperoxides when compared with reference sample – 1b may be observed. The light initiated ageing (day light 1000 Wm\(^{-2}\) leads to the crumbled sample – 3b. Polyester urethane is less affected by the heat induced oxidation – 2a while the light initiated ageing – 3a leads to a significant yellowing.

The effect of nitrocellulose ageing on DSC exotherms may be seen in the Fig. 2.

![DSC runs in nitrogen (the rate of heating 5 °C/min) of aged samples of nitrocellulose. The numbers at respective line denote the days of the sample ageing at 130 °C in air.](image)

The pronounced extent of ageing leads to the reduction of DSC exotherm. This was attributed to the gradual loss of nitro group.

Under certain conditions of ageing (humidity, initiation by light) an increased amount of carbonaceous residue found under nitrogen by nonisothermal thermogravimetry at 550 °C was observed and was linked to an increasing extent of crosslinking in an aged sample.

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Evaluation of the decay degree of *Tilia cordata* wood by different analytical methods

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Lime wood samples decayed under the attack of the white rot fungus *Phanerochaete crisosporium*, for different durations, have been obtained. The degree of decay was determined by mass loss and the samples were analyzed by different analytical methods (FT-IR spectroscopy, 2D IR correlation spectroscopy and thermogravimetry).

The modifications of the wood due to presence of the fungus were assessed by comparing the structural features of decayed lime wood samples with references. The relative changes in intensities of spectral bands associated with lignin and carbohydrates as a result of decay were determined after different exposure periods. The differences between reference and decayed wood spectra were examined in detail using 2D correlation spectroscopy and the second derivative analysis. Thermal properties both with respect to wood hydrophilicity (evidenced mainly in the desorption process) and decomposition behavior were evaluated.

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Polyolefins with the simplest chemistry of most synthetic polymers still demand a superior and multidisciplinary effort in its microstructure characterization.

Besides the molar mass distribution, there exists a wide range of significant structural features in the polyolefin molecular architecture such as:

- the presence of short chain branches, by the addition of a comonomer, could result in homogeneous incorporation. If it is not the case, we need to deal with a short chain branching distribution which also leads to an often complex molar mass – composition interdependence.

- the presence of long chain branches, which even in small quantities have a significant influence in rheological properties.

- stereoregularity differences in the case of polypropylene.

And very often, with the goal of optimizing final product performance, the industrial polyolefin products are a complex combination of resins with the features above.

It is not surprising that various separation techniques are required to cover those needs and all of them have to face the good chemical resistance of polyolefins, thus demanding operation at high temperature to bring the resin in solution which adds complexity to the instrumental technique operation.

A review of the newest techniques developed in the recent past years such as:

- Crystallization elution fractionation
- Cross fractionation chromatography
- High temperature solvent gradient and thermal gradient interaction chromatography

will be presented with most recent work in terms of application and instrumentation.
2D-LC Characterization of Branched Polymers

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Size exclusion chromatography (SEC) fractionates polymer molecules utilizing the distribution of polymer molecules between common solvents located at the interstitial space and the pore volume of the porous column packing materials. The distribution equilibrium is mainly governed by the conformational entropy difference of the polymer chains in the two different physical environments. In results, SEC separates the polymer molecules in terms of the size of a single polymer molecule in the elution solvent. Therefore SEC is inefficient in the separation of branched polymers according to the molecular weight (MW) since the chain size not only depends on molecular weight but also depends on the chain structure. Nonetheless, by virtue of its sensitivity to the chain size, SEC can distinguish the branched polymers from that of a linear polymer with equivalent MW. A quantitative description of chain size contraction with branching was developed by Zimm and Stockmayer long ago and it has been utilized widely to estimate the chain branching using SEC/multiple detection system.

In contrast to SEC, interaction chromatography (IC) utilizes mainly the enthalpic interaction, adsorption or partition of solute molecules to the stationary phase, and it is sensitive to molecular weight not the size. In addition, band broadening is far less serious in IC than SEC. IC can separate the branched polymer according to MW more or less independent of long chain branching. Therefore, combination of two LC techniques, one is sensitive to chain size and the other is sensitive to MW, can provide a unique tool for in-depth branching analysis. In this presentation, our recent work on the analysis of branched polymers will be presented.
Statistical Two-Dimensional NMR: Assignment of Complicated Resonances Due to the Carbonyl Carbons of Methacrylate Copolymers

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NMR spectra of multi-component copolymers usually show complicated splitting due to monomer sequences and stereoregularity, and thus direct analysis of those spectra is troublesome. Recently, we reported that methods of multivariate analysis were useful to extract quantitative information about chemical composition and monomer sequence distribution from $^{13}$C NMR spectra of methacrylate copolymers\textsuperscript{1} and terpolymers.\textsuperscript{2} The results encouraged us to develop a new method to make assignments of the complicated resonances due to copolymers with the aid of statistical treatments.

Statistical two-dimensional correlation spectroscopy, based on correlation coefficient mapping first proposed by Barton II et al.\textsuperscript{3} has been developed in some spectroscopic studies such as IR and mass spectroscopies.\textsuperscript{4} This method was also applied to NMR-based metabolomics, in which statistical homo- and heteronuclear correlations were shown, for instance to decipher the structure of many metabolites from biofluid samples.\textsuperscript{5,7}

Copolymers of methyl methacrylate (MMA) and $t$-butyl methacrylate (TBMA) with varying stereoregularity were prepared by radical copolymerization in ethyl lactate at $-40$ °C. \textbf{Fig. 1.} $^{13}$C NMR spectra of the carbonyl carbons of poly(MMA-co-TBMA)s prepared at $-40$ to $40$ °C, and of PMMAs derived from the copolymers (in CDCl$_3$ at 55 °C, 100 MHz).
to 40 °C. The copolymers had chemical compositions ranging from 51.2 to 55.9 % in TBMA unit content. The poly(MMA-co-TBMA)s were converted to PMMAs by hydrolytic cleavage of the t-butyl functions and subsequent methylation with diazomethane.

Fig. 1 shows $^{13}$C NMR spectra of the carbonyl carbons of four poly(MMA-co-TBMA)s and four PMMAs derived from the copolymers. NMR spectra of the PMMAs indicated that relative intensity of the signal of syndiotactic pentad (rrrr) increased as the polymerization temperature decreased. On the other hand, difference in the $^{13}$C NMR spectra of the poly(MMA-co-TBMA)s was not obvious, although the cotacticity of the copolymers should vary significantly with the polymerization temperature as well as the converted PMMA.

Fig. 2 shows 3D plots of the covariances of the bucket-integral data set for the $^{13}$C NMR signals due to the carbonyl carbons of poly(MMA-co-TBMA)s and of the PMMAs derived from the copolymers. Positive correlations were observed on the straight line; at 176.51-176.63, 176.71-176.91, 177.01-177.13, 177.65-177.73, 177.87-177.99, and 178.23-178.27 ppm of poly(MMA-co-TBMA)s against 177.51-177.77 ppm of PMMAs. Based on the fact that the signal at 177.63 ppm is assigned to the rrrr pentad stereosequence in PMMA, statistical 2D NMR method succeeded in selectively extracting the signals of rrrr stereosequences in PMMA, statistical 2D NMR method succeeded in selectively extracting the signals of rrrr stereosequences in the copolymers from the complicated spectra of the copolymers.

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Characterization of UV Curable Multimodal Oligomers Using a Semipreparative GPC Method Combined with a Triple Detection System

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In the last decade, many review and articles have been published reporting methods for preparing UV curable powder coatings, printing inks, pressure sensitive adhesives (PSA) and biocompatible polymer gels [1]. These UV curable polymer materials are conventionally constituted by difunctional or trifunctional methacrylated monomers combined with some oligomers, such as polyethyleneglycol-dimethacrylate (PEGDMA), bisphenol-A-propoxylated-dimethacrylates (BPA-P-DMA), polyurethane-di-(meth)acrylates and polyester-di-(meth)acrylates (PUDMA). Under UV curing treatment in presence of a photoinitiator, the generated network is strongly dependent on UV doses, difunctional to trifunctional monomer ratios, photoinitiator efficiency and the chemical nature of the oligomer. In particular, the most UV curable mixtures are based on (BPA-P-DMA) oligomers, which are commercially well-known as epoxymethacrylates (EPDMA), providing fast photocrosslinking reactions and good mechanical properties in coatings, varnishes and adhesives. Many different types of EPDMA are available and the main difference of these oligomers are in the polymer architecture showing i) linear chain having methacrylated groups at the chain end oligomer or ii) branched macromolecules, where these branches are randomly distributed showing many different branching points or variable branch lengths, attached not only to the backbone, but to the branches as in the case of UV curable oligomers having relatively high molecular weights. As reported in Fig. 1, a rather complex molecular weight distribution can be observed in case of relative high molecular weight, where multimodal distribution have been detected [2]. Furthermore, the final mechanical properties of the UV cured coatings are strongly influenced by the EPDMA macromolecular architecture generating brittle or though photocrosslinked polymer matrices in case of low or relatively high molecular weights, respectively. The conventional approach by using a column calibration with polystyrene standards cannot be applied for complex multimodal molecular weight distributions, while by using an advanced multi-detection GPC system, such as the Viscotek TDAmax equipped with a light scattering and a concentration detectors (RI and UV), absolute molecular weight measurements for each slice of the chromatogram can be determined. When a differential viscometer is also included in the Viscotek TDAmax, used to measure the intrinsic viscosity (IV) of oligomers in a multi-detection SEC system, an additional information in the hydrodynamic radius can be also obtained to calculate the chain branching degree. Four different samples of EPDMA oligomers were characterized with a Viscotek TDAmax system,
equipped with two PL Resipore columns Mixed D 300x7.5 mm, where one sample was quasi-linear oligomer (i.e. low branching degrees) and other three ones were randomly branched showing medium (mid-br) and high branching (high-br) degrees. The samples were eluted from the GPC system, in a THF solvent, operating at a flow rate of 1.0 mL/min at 35°C. The molecular weight, intrinsic viscosity, and Stokes radius for each oligomer were calculated directly from the Viscotek OmniSEC software. The branching average degree and frequency were also calculated from the OmniSEC software, using the Mark-Houwink (MH) plot obtained by log(IV) vs log(Mn). A typical GPC raw data can be analyzed in the different retention volume range (see black arrows in fig. 1) by using OmniSec software for a rough estimation of number average molecular weights and the branching degree. The triple detection system can be also applied with a multimodal molecular weight distribution, but a detailed characterization requires a further separation of the chromatographic peaks. The complete separation of chromatographic peaks can be obtained with a semi-preparative GPC technique by using a mixed Mixed D 300x25.0 mm PL columns eluted with THF with a flow of 8 ml/min due to an isocratic pump (Knauer K501), and an UV detector. The results of the semi-preparative GPC fractionation can be also obtained with a semi-preparative GPC technique by using a mixed Mixed D 300x25.0 mm PL columns eluted with THF with a flow of 8 ml/min due to an isocratic pump (Knauer K501), and an UV detector. The results of the semi-preparative GPC fractionation can be reported in Table I, where the multimodal chromatogram shown in fig.1 can be separated into seven different fractions. For each fraction were calculated both the polymerization degrees (Xn), by measuring the 1H-NMR spectra, and the theoretical Mn (Mnth) assuming oligomer with linear chains. The Mnth were compared with those obtained by the triple detection GPC system (i.e. MnthGPC) calculated separately for all seven fractions derived from semipreparative GPC fractionation. The comparisons between two molecular weights, obtained with (MnthGPC) and without fractionation (Mnth) (see Table I) show that a large deviation between two data sets is observed with polymerization degrees above 6. These results are in good agreement with MH analysis which predicts a high branching degree for oligomers with a polymerization degrees above 6.

In conclusion, the combination of semipreparative GPC and a triple GPC detection system is a powerful experimental approach to determine the branching degree and Mn of complex multimodal molecular weight distributions. The same approach will be extended to other commercially available oligomers, such as epoxy, phenolic and unsaturated polyester resins.

### Table I. Some comparisons between the obtained results with semi-preparative and conventional GPC using the triple detection system.

<table>
<thead>
<tr>
<th>Fraction nr</th>
<th>a)Xn</th>
<th>b)Mnth</th>
<th>c)MnthGPC</th>
<th>d)PDI</th>
<th>e)Mnth</th>
<th>f)PDI</th>
<th>g)BD</th>
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<tr>
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<td>6813</td>
<td>1.109</td>
<td>3425</td>
<td>1.131</td>
<td>46.0</td>
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<tr>
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<td>2730</td>
<td>4681</td>
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<td>3425</td>
<td>1.131</td>
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<tr>
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<td>2287</td>
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<td>1.035</td>
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<tr>
<td>4</td>
<td>6.6</td>
<td>2108</td>
<td>1981</td>
<td>1.030</td>
<td>1879</td>
<td>1.006</td>
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<tr>
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<td>3.9</td>
<td>1336</td>
<td>1189</td>
<td>1.006</td>
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<td>691</td>
<td>481</td>
<td>1.001</td>
<td>410</td>
<td>1.101</td>
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<tr>
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<td>1.3</td>
<td>583</td>
<td></td>
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</table>

a)Polymerization Degree calculated by using molecular weight of repeating units and chain ends of 280 and 254 g/mol, respectively; b) Number Average Molar Mass by 1H-NMR; c) Number Average Molar Mass by GPC and Polydispersity Index after semipreparative GPC fractionation; d) Number Average Molar Mass and Polydispersity Index of oligomers without semipreparative GPC fractionation of oligomer; e) percentage branching degree calculated with MH equation constants.

### References

Polyethylene (PE) is one the worlds most widely used polymers and despite its simple structure finds its way into our everyday life in many applications, from pipe lining and wire coatings to shopping bags. The properties of the material are highly dependent on the molecular weight and analysis of this parameter by gel permeation chromatography (GPC) is vital for research and quality control. Triple Detection GPC, using a differential refractometer (RI), right angle light scattering (RALS), low angle light scattering detector (LALS) and differential viscometer detector is a very powerful technique for the determination of absolute molecular weight and structure. The presence of long chain branching (over 6 carbons in length) in polyolefins influences to a great extent physical properties such as melt viscosity and mechanical strength. The polymerization mechanism directly effects the distribution of chain branches in polyolefins and the determination of this is of significant interest in the production of materials with well-defined and characterized molecular weight and branching distributions for specific applications.

In this poster, we demonstrate the capabilities of the Viscotek High Temperature Triple Detection GPC (HT-GPC) in measuring the absolute molecular weight and the study of its structure, without the need for column calibration that is required for the Universal Calibration method.
Pitfalls in the Interpretation of the Results of SEC Measurements

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The interpretation of the results of size-exclusion-chromatography (SEC) measurements is subject to a number of complicating factors requiring corrections, such as band broadening due to eddy diffusion, longitudinal or axial diffusion [1], concentration effects [2], flow-rate stability [3], etc. In the present communication, we focus on two of those which often result in the serious misinterpretation of experimental data, viz., the improper use of polystyrene calibration and the problems of identification of minority components in polymer analytes.

In the very frequent case when the SEC set is not equipped with a molecular-weight-sensitive detector, the molecular weight of the eluate at a particular elution volume, $V_{el}$, is assessed using the calibration line. By calibration line is meant the dependence of molecular weight, $M$, of the polymer to be analysed on the elution volume. For non-common or newly synthesised polymers suitable standards of that polymer with narrow molecular-weight distribution (MWD) in a desirably broad range of molecular weights are mostly not available. One has to resort to a standard polymer which is constitutionally different from the analyte but is available as a kit of linear samples with narrow MWD covering a broad range of molecular weights. The requirements are fulfilled mostly by polystyrene (PS) and poly(methyl methacrylate) standards, the former being used predominantly [3].

If a polymer different from polystyrene is analysed and the elution curve is evaluated using calibration by linear PS standards for the given SEC set, the molecular weights calculated are generally not true $M$ values of the polymer analysed but values that should be called ‘polystyrene-equivalent molecular weights’, i.e., molecular weights of polystyrene eluted at a particular elution volume. A PS-equivalent $M$ would typically differ from a true $M$ by ten to twenty per cent [4]. For highly branched polymers, the difference can be a multiple. If the slopes of the calibration lines for the analyte and linear PS, in the co-ordinates $\log M$ as a function of $V_{el}$, are different, then not only the $M$ values but also the width of the molecular-weight distribution can be different from the true value.

The problem of using for the evaluation of SEC data calibration by a polymer different from the analyte can be mitigated somewhat if, for both polymers, the parameters are known for the Mark-Houwink equation describing the dependence of intrinsic viscosity, $[\eta]$, on molecular weight, $M$, and assuming the validity of the universal-calibration theorem. Then, the calibration for the standard polymer can be recalculated in the calibration dependence for the analyte.
The second pitfall into which credulous experimentalists often fall is the belief that unimodal, nearly symmetrical SEC elution curves prove the one-component character of the polymer analysed. The potential presence of minority components is of serious concern with block and graft copolymers, as well as with other polymers prepared by multi-step syntheses. In the individual reaction steps, the conversion is never total and the complete removal of the unreacted starting substance is difficult, if not impossible. It is sensible to assume that in the product of a multi-step synthesis some remnants of all intermediate products are present. The final product is usually characterised by SEC. Unless a second peak, or at least an indication of a second inflection point, appears, it is mostly assumed that the final product is only the substance aimed at.

To check this, we have developed an algorithm for the simulation of SEC elution curves for multi-component polymer systems [5]. Using the algorithm, the shapes of the overall SEC curves with a wide range of parameters describing binary and multi-component polymer systems were generated. The crucial parameters determining the shape of the elution curves are: (i) the ratio of the molecular weights of the components; (ii) the breadth of the molecular-weight distributions of the components; (iii) the mass fractions of the components; (iv) the band broadening.

A detailed scan of the multi-dimensional space with the above variables leads to the following qualitative conclusions:
1. Identification of minority components in multi-component polymer systems is much more difficult than has been generally assumed.
2. Understandably, the identification of the presence of a minority component is the easier the larger is the ratio of molecular weights of the components, $M_1/M_2$.
3. Understandably again, the identification of the presence of a minority component is the easier the narrower are the molecular-weight distributions of the components.
4. Even for narrow MWD of both components, such as $M_w/M_n \sim 1.1$, and the ratio of molecular weights of the two components $M_{n,2}/M_{n,1} \sim 2$, the minority component manifests itself only if its mass fraction $w_1 > 0.1$.
5. Two inflection points on the elution curve of a binary polymer system only appear if $M_{n,2}/M_{n,1} > 2$ or $M_{n,2}/M_{n,1} < 0.5$, and the mass fraction of the minority component $w_2 \geq 0.1$.
6. The much desired base-line separation can only be achieved for components with narrow MWD and greatly differing in molecular weighs, e.g., $M_{w,i}/M_{n,i} < 1.1$ and $M_{n,2}/M_{n,1} > 5$.

References
Tensile Modulus, Poisson Ratio, Storage Modulus, Indentation Modulus and PALS analysis of Polypropylene/Cycloolefin Copolymer Blends

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Object of this presentation is a summarizing report on PP/COC blends focusing attention on mechanical and micromechanical analysis in relation to the composition and Free Volume Holes (FVH), as evaluated from Positron annihilation lifetime spectroscopy (PALS).

Isotactic polypropylene (MFI = 5.7 ± 0.1 dg/min at 230°C, 2.16 kg; density: 0.90 g/cm³; Lyondell-Basell, Ferrara, Italy) and an amorphous cycloolefin copolymer COC Topas 8007 (MFI = 11.3 ± 0.6 dg/min at 230°C, 2.16 kg; density: 1.0 g/cm³; Tg = 80°C; Ticona, Celanese, Germany) were mixed in a Banbury mixer at 190°C for 3.5 min and a series of COC/PP blends was prepared with 95, 90, 85, 80, 75, 70, 60, 50 and 25 weight % of PP. Then testing ISO 527 (170 mm; 4 mm; 80 mm; 10 mm) specimens were produced by injection moulding (melt temperature: 230°C; injection pressure: 30 MPa; mold temperature: 50°C).

The effect of COC stiffening in PP matrix was compared at various composition taking into account the specific behaviour at room temperature of a semicrystalline and an amorphous glassy polymer.

Experimental measurements include determination of:

- Tensile modulus and Poisson Ratio (Fig.1) were measured as average on five specimens, according to ASTM D638-10 by using a bi-axial extensometer at 5 mm/min;

![Figure 1](image)

- Indentation Elastic Modulus (Eit) was measured with the tester DUH211S by using the equation (1)

\[
\frac{1}{E_{t}} = \frac{(1-v_{t}^2)}{E_{t}} + \frac{(1-v_{i}^2)}{E_{i}}
\]  

(1)
where $E_r$ is the experimental reduced elastic modulus based on indentation contact, $v_s$ is the Poisson ratio of specimen, whereas $E_i$ and $v_i$ are the Young's modulus and Poisson's ratio for indenter, respectively.

- Storage and loss modulus were measured in bending configuration at various frequency (0.3-50Hz) in the interval -50/150°C; the activation energy at the glass transition temperature was also measured.
- Heat Deflection Temperature (at 1.8 MPa and 2°C/min) increased from 62°C for PP, to 79, 82, and 83°C for 25, 50 and 100% by wt. of COC respectively, confirming the stiffening role of COC.
- Positrons, from a 30 µCi $^{22}$NaCl source, interact with electrons and may form positronium (Ps), localized in a free-volume hole (FVH). The triplet ortho-Ps ($o$-Ps) annihilation depends on the FVH dimension and concentration. The pick-off annihilation lifetime of the $o$-Ps ($\tau_{o-Ps}$, expressed in ns) is directly correlated to the size of the free-volume holes by the semi-empirical equation

$$\tau_{o-Ps} = 0.5\left[1 - R/(R + \Delta R) + (2\pi)^{-1} \sin(2\pi R/(R + \Delta R))\right]^{-1}$$

(2)

where $R$ is the radius of the spherical free-volume hole (FVH) where the pick-off annihilation lifetime of $o$-Ps is measured, and $\Delta R = 0.1656$ nm is an empirical constant.

Fig.1A shows experimental tensile modulus of ISO 527 samples, whereas Fig. 1B evidences the correspondent Poisson ratio at room temperature. Other experimental measurement of storage modulus and indentation modulus show similar dependencies on the composition and on the blend density. In the same time, PALS analysis evidences the relationship of free volume with the composition. In particular the unperturbed by the positron irradiation $o$-Ps intensity $I_3(0)$ is reported in Fig.2A. Moreover, Fig.2B shows the mean FVH radius $R$ and its standard deviation (STD of $R$) calculated from eq. ( ) as a function of the COC content in PP. The dash line represents the simple additive rule.

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The significant increase of the competition in the sector of specialty chemicals, in particular in the field of polymers, drives industrial scientists to develop and use tools which allow the acquisition of more accurate, reliable and robust basic data. Many technical approaches can be used in order to obtain conversion or molecular weight during a polymerization reaction. Discrete withdrawal of aliquots allows one to use off-line techniques like gas or liquid chromatography, Nuclear Magnetic Resonance (NMR), etc. However, such chromatographic systems or NMR instruments necessitate a tedious sampling and preparation such as extraction, dilution or filtration, etc. Moreover, they are usually the analytical equipment is costly to implement and maintain. In order to overcome these limitations, one can use Automatic Continuous Online Monitoring of Polymerization reactions (ACOMP).\textsuperscript{1,2} It provides automatically a high number of data points and allows comprehensive, model independent monitoring of (co)monomer conversion, weight average molar mass $M_w$, weight average intrinsic viscosity $\eta_\text{inv}$, average composition drift and distribution (for copolymers), and certain measures of polydispersity. Hence, this technique is a very powerful tool for quantifying kinetics and mechanisms that currently are often left to conjecture and eventually lead to the ability to control the process during the polymerization reaction.

Fig. 1 Molar conversion of acrylic acid as a function of time obtained at various pH. Inserted is the variation of the initial rate of polymerization as a function of the pH.
In this communication, we present the use of ACOMP to revisit the free radical polymerization at high temperature, i.e. up to 98°C, of acrylic acid in aqueous solution of various pH. This monomer is widely employed in the industry for the preparation of, for example, super absorbents, thickening agents and dispersants. As expected, in figure 1, ACOMP allows one to observe the dramatic effect of the increase of the pH on the polymerization rates ($R_p$), i.e. a decrease up to pH ~6 and then follow up by an increase in $R_p$. This is due to the balance between electrostatic and osmotic repulsions.

$$y = -146059x + 40.774$$
$$R^2 = 0.9988$$

Moreover, we used the same technique to monitor the thermal decomposition of the initiator system at various temperatures and pH conditions. To our knowledge this is the first work which highlights the possible use of this technical approach to gain basic kinetic data of unimolecular decomposition reactions. We used this data to confirm the presence of a sufficient concentration of primary radicals within the reaction solution during the whole experiment. The obtained activation energy of the thermal decomposition rate coefficient ($k_o$) is in good agreement of the expected value$^3$ (cf. Fig 2) which was subsequently employed to obtain the ratio of the propagation to the termination rate coefficients ($k_p/\sqrt{k_t}$).

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From New Materials to a Complete Device.
The Role of Characterization Techniques in the Development of Novel Polymeric Solar Cells.

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Thin-films solar cells based on organic and polymeric photoactive materials represent one of the most promising technologies to afford low-cost, readily available energy. In the last years a large number of academic groups and industrial companies have started research programs aiming to find and develop new active materials and to optimize the device architectures; the final goal is to achieve efficient, durable and cheap solar cells that can enter the market of photovoltaics, especially for niche applications.

Polymer solar cells (PSCs) are layered devices where a thin film (50-200 nm) of a photoactive material is sandwiched between an anode and a cathode. In the state-of-the-art devices, the photoactive material consists of a blend of a conjugated polymer and a functional fullerene; the first component (electron donor) is able to absorb the sunlight and generate an hole-electron pair (exciton) which migrates toward the interface with the second component (electron acceptor) where it is dissociated, causing the transfer of an electron from the donor to the acceptor, provided that the energy levels of HOMO and LUMO are correctly matched. The donor-acceptor blend should exhibit a dispersed morphology (bulk heterojunction), where the interface between the two materials is maximized to favour the photoinduced electron transfer, but that at the same time retains an interpenetrating network structure to assure percolating paths for the separated charges (holes and electrons) to the electrodes (anode and cathode, respectively).

The optimization of PSCs encompasses the development of new approaches in the design of materials and of device architectures. Materials research in this field focuses mainly on the preparation of materials with broad absorption, ideal energy levels matching, high charge mobility, controlled morphology, stability to oxidation, to be used as the photoactive layer.

Usually, buffer materials are interposed between the active layer and one or both the electrodes. They are used to suppress charge recombination, to transport/block electron/holes, to tune the electrodes work function, to render more ohmic the active layer/electrodes interfaces, to act as optical spacers.

The electrodes assure photogenerated charges collection and the difference of their work function is the driving-force for the charge carriers migration by generating a built-in potential. The cathode is usually a low work function metal (e.g. aluminium) or a metal pair (e.g. Ca/Al), whereas a high work function material is used for the anode. Transparent conductive oxides (TCOs), especially tin-doped indium oxide (ITO), are the most commonly used material to this end. One of the electrode must be

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transparent, to allow the light to reach the active layer. In most cases ITO is the transparent electrode, but very thin metallic layers (<20 nm) can also be employed for this purpose.

From all this it follows that despite the complexity of solar cells devices, from the synthesis and choice of each component to the design of the architecture and the final assembly, disposing of information given by suited characterization techniques is of great help in taking decisions intended to improve the devices performances. Characterization of the single components as well as of the final device constitute a central issue when aiming to progress in this field.

Along with researchers’ general increase of knowledge of this technologically interesting objects, there is a constant development of the ability of applying traditional characterization techniques, on one side, and, on the other side, setting up ad-hoc equipment and characterization methods.

In the present lecture the most relevant techniques will be presented following the “history” of a solar cell, from the choice of its polymeric components to the characterization of the final device and the evaluation of its behaviour upon time and sun exposure.

As the process that leads to the realization of a solar cell is long and time consuming, and requires a considerable number of optimization procedures at different levels, it is common practice to perform a previously a screening on the materials to be employed in order to reduce the number of trials on the basis of the actual know-how. In particular, a selected polymeric material undergoes physico-chemical analysis, photophysical, morphological and mobility study, in order to assess its suitability to be employed for a certain role. The complete device itself is then analysed to give useful data to be used in a sort of “feedback” process that helps to perfection the criteria used to establish, as earlier as possible in the decision procedure, how to select the materials and, at a higher level, to choose the practical fabrication techniques that can best lead to a performing device.

Non exhaustive survey of characterization techniques commonly used in PSC research. Observables and information that can be obtained are also mentioned.
Controlled Crystallization in Semiconducting Polymer Thin Films

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During the last decade π-conjugated polymers like poly(3-hexylthiophene) (P3HT) have attracted great attention as active layers in low-cost electronic and optoelectronic devices such as organic field-effect transistors and solar cells. Highly regioregular poly(3-hexyl thiophenes) tend to strong crystallization which results in anisotropic charge transport. Charge-carrier mobilities and overall device performance are strongly dependent on polymer morphology comprising chain alignment, nucleation density and crystallinity. It is of great interest to gain simultaneous control of these parameters and get an in-depth understanding between the morphology and the macroscopic charge transport.

We recently established a method of controlled dissolution and recrystallization of pre-formed, i.e. spincoated P3HT films swollen to a well defined degree in vapours of a good solvent.1 The effective polymer concentration (ratio of initial thickness to swollen thickness) in the thin film concentrated solution is controlled by the relative solvent vapour pressure while in-situ optical microscopy under crossed polarizers or optical spectroscopy can identify the conditions (concentration) at which the polymer crystals completely dissolve. Recrystallization proceeds by a nucleation and radial growth of spherulitic domains familiar from classical semicrystalline polymers comprising nanocrystalline lamellae emanating radially from the nucleation centre.

Controlled nucleation and growth allows reduction of the nucleation density, i.e. increased spherulite diameter (10 to 100 µm), to such an extent that a transistor channel can be placed entirely within a well oriented domain, enabling us a direct measure of transport anisotropy in these structures.2

We further couple the low nucleation density to confined geometries produced by soft lithography in order to gain well-ordered and aligned structures over macroscopic distances. Ultimately this allows us to study the relationship between the polymer microstructure and the resulting charge transport properties.

References

1. INTRODUCTION

The biodegradability and compostability of plastics and of packaging are defined, not only by technical standards, but also by laws. Thus, it is a sector in which there is a limited margin for subjective interpretation, and it is possible to work in a transparent fashion.

Biodegradable plastics are not developed in opposition to traditional polymers, but to satisfy a number of specific applications. Two typical examples are the compostable bags for the collection of organic waste and the biodegradable mulching films for use in farming. In both cases, biodegradability is a factor that improves both the product and the practice “performance”. As a biodegradable plastic is indistinguishable from a non-biodegradable plastic, it was necessary to develop a process for defining the criteria for the quality, which, in this case, are criteria of environmental quality, together with the process of industrial innovation. Consequently today we can speak about biodegradable plastic materials and compostable packaging, using terms that have been formalised as standards and specific laws.

2. THE HARMONISED STANDARD EN 13432

The European standard EN 13432 “Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging”, defines the characteristics of packaging that may be recycled through organic recycling. This standard, which has been unanimously approved by the national standardisation bodies, was subsequently supported by the European Commission. EN 13432 is a harmonised standard, that is, it has been mentioned by the Official Gazette of the European Communities (L 190 12/07/2001 p.0021-0023) as the standard for implementing the European Directive on packaging and waste from packaging (94/62/EC). As such, it indicates conformity to the essential requirements of packaging (with respect to “packaging recoverable in the form of compost” and “biodegradable packaging”), in accordance with the European Directive and, in particular, with the national laws implementing the Directive.

EN 13432 is currently a reference norm for the manufacturers of biodegradable materials, public authorities, composters and consumers.

According to EN 13432, "biodegradable and compostable" packaging must have the following characteristics:

- Biodegradability,
- Absence of negative effects on the composting process.
- Low levels of heavy metals (below preset maximum values) and absence of negative effects on the quality of the compost (e.g.: reduction of the agronomic value, and presence of eco-toxicological effects on plant growth).

Each of these points is necessary for the definition of compostability, but, alone, they are not sufficient.
At International level the standard of reference is the ISO 17088 (*Specifications for compostable plastics*). The general approach and requirements of the ISO 17088 are practically identical to the EN 13432.

3. CERTIFICATION

Standardisation has the specific role of “giving order to a particular context”, as indicated in EN 45020. In the context of compostable products, order has been achieved over the last few years with the introduction of definitions and test methods, thanks to which, the expression “biodegradable and compostable” is no longer abstract and impractical, but can be used to define the specific, particular, measurable and verifiable properties of products that are put on sale, because it is now associated with a reference standard. The next step is to provide the consumer with a system for recognising compostable products, by means of a visible label on the product itself. The label has the dual role of identifying the products that conform to the standard, and of guaranteeing the fact that the products have been assessed and are controlled. All of this can be achieved by means of certification and control by third parties.

Historically speaking, the first certification organisation to implement a programme of certifying the compostability of plastics and of packaging was Vinçotte (Belgium), which also created a specific label, “OK Compost”. DINCertco (Germany) followed soon with its certification programme. In Italy first certifications were carried out by the I.I.P. and most recently the CIC (Italian Composting Association) started a new certification programme to assure the quality of the materials delivered to the composting plants.

4. CONCLUSIONS

The work carried out in the 90’s in the field of biodegradable plastics overcame the uncertainties and difficulties in the beginning, when the terms biodegradable and compostable were not associated with an operating definition or with any specific, reliable test method.

We now have definitions, test methods, and materials actually on the market, and it is, therefore, possible to operate in this sector transparently, using objective references. Full, and above all, lasting commercial development of new applications, such as biodegradable plastics, can only be achieved if we ensure high levels of quality, which, in this case, primarily means environmental quality. Thus, standardisation, in association with certification of conformity, is essential in the field of technological innovations.
In recent years, new nanoporous crystalline polymeric materials based on syndiotactic polystyrene (sPS) have been discovered and extensively studied. sPS is able to form co-crystalline phases with several low-molecular mass guest molecules and, by suitable guest extraction procedures, two nanoporous crystalline forms named $\delta$ [1] and $\varepsilon$ [2] can be obtained. The $\delta$ form presents two identical cavities per unit cell while the $\varepsilon$ form is characterized by channel-shaped cavities crossing the unit cells along the $c$ axis (see Figure 1).

**Figure 1:** Representation of the nanoporous $\delta$ and $\varepsilon$ crystalline phases.

Both crystalline frameworks rapidly absorb volatile organic molecules (VOC), even if present in traces in air or water and hence are promising for applications in chemical separations and air/water purification [3]. Moreover, the use of these materials as sensing elements for volatile organic compounds in molecular sensors [4] and for active packaging of fruit and vegetable has been also proposed [5].

Recently, it has been also shown that porous aerogels can be obtained by supercritical CO$_2$ extraction of the solvent present in sPS physical gels.[6] The porosity, as well as the morphology and the crystalline structure of the aerogels can be easily controlled by suitable preparation procedures. [6]
It has been observed that sPS aerogels with a nanoporous crystalline phase present the high guest sorption capacity of other nanoporous crystalline samples (i.e. powder and film) associated with a much higher guest diffusivity [6b] and a possible use of nanoporous sPS areogels for hydrogen storage has been investigated [7].

The lecture introduction will briefly present the different materials considered for hydrogen storage with particular emphasis to porous polymers. Then, the literature information relative to sPS polymorphism will be given. The second part of the lecture will focus on the sorption properties of sPS materials characterized by crystalline nanopores and data concerning the hydrogen sorption will be presented. In the final part of the lecture, the possibility to obtain nanoporous crystalline phases with other polymers will be discussed and preliminary results obtained with poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) will be reported [8].

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Hyphenated DSC and Raman to provide deep insight in polymer structure

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Differential Scanning Calorimetry (DSC) is a well known technique to quantitatively assess different properties of polymers such as glass transition, melting point, degree of crystallinity and others.

RAMAN spectroscopy is a useful technique which can qualitatively give important information at the molecular level on the structure of the material, as it investigates the low frequency modes of the molecule.

This means that DSC and RAMAN are complementary techniques and therefore it can be very useful to combine them into a single instrument.

Here we present a few results on different kind of polymers (thermoplastics and thermosetting) that show the ability of such a hyphenated technique to provide valuable information on the evolving structure of a polymer.
Studies of nanostructured diblock copolymer systems using small-angle scattering in transmission and grazing incidence geometry

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Abstract  Diblock copolymers can self-assemble into regular nanostructures on the length scale of 10-100 nm due to repulsion between the two chemically dissimilar blocks joined by a covalent bond. The phase-behaviour of diblock copolymer melts is controlled by a number of parameters, i.e. the interaction energy between the two blocks, the relative size of the two blocks, and the overall degree of polymerization, i.e. molar mass. Phase diagrams for common systems featuring many different structures with long-range order, are well documented\textsuperscript{1}. Small-angle scattering, SAS, is well suited to study the structure of such systems: With a wavelength $\lambda \sim 1$ Å of the diffracting radiation (x-rays or neutrons) and a repeat distance, $d$, of the long range ordered system under investigation, in the range 10-100 nm, Bragg's law $n\lambda = 2d \sin \theta$, where $n$ is the order of the diffraction peak, gives a typical scattering angle, $2\theta \sim 1^\circ$. Studies of bulk diblock copolymer systems using small-angle x-ray\textsuperscript{2} and neutron scattering\textsuperscript{3} (SAXS/SANS) in transmission geometry are presented\textsuperscript{4}.

Diblock copolymer thin films are potential candidates for preparation of e.g. nanoporous films, nanostructured templates, photonic crystals and biosensors, and it is thus important to characterize the structure throughout the film. SAS in reflection geometry, grazing-incidence small-angle scattering, GISAS, enables such studies of the inner film structure both along the thin film normal and in the film plane. A brief introduction to the technique and analytical possibilities is given\textsuperscript{6}. Figure 1 shows an Atomic Force Microscopy (AFM) picture of a thin lamellar poly(styrene-$b$-butadiene) P(S-$b$-B) diblock copolymer film together with the corresponding GISAXS map. Bragg rods appear at $+/-.008$ Å$^{-1}$ as expected from the AFM picture showing a perpendicular orientation of the lamellae. The corresponding repeat distance of 78.5 nm is consistent with the value from bulk SAXS. GISAXS at synchrotron radiation facilities allow time-resolved data to be obtained with a time-resolution of
~ 10s. GISAXS data allowing the structural rearrangements in a lamellar P(S-b-B) thin film during treatment with solvent vapour to be followed in time, will be presented and discussed.7,8.

**Figure 1.** A thin film P(S-b-B) with a molar mass of 183 kg/mol, bulk lamellar period of 83.9 ± 1.3 nm, and a film thickness of 232 nm. To the left tapping mode AFM height image. Image size is size 3 m x 3 m. The vertical scale between darkest and lightest parts of the image corresponds to 80 nm. To the right GISAXS intensity map on a logarithmic scale. The incident angle was 0.20° at a photon energy of 8 keV. The vertical stripe down the middle of the GISAXS pattern is the shadow of the beamstop. Straight Bragg rods at \( q_z \) of 0.008 Å\(^{-1}\) indicate the formation of perpendicular lamellae (data presented in ref. 9).

**References**


Block copolymer vesicles as chemical nanoreactors and molecular release systems: The characterization challenge

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Containers of microscopic or nanoscopic size are promising candidates as carriers in molecular and drug delivery, as nanocontainers in catalysis and as ultra-small reaction vessels [1]. Block copolymers exhibiting amphiphilic character can self-assemble into vesicles in dilute solution [2], and can be used to encapsulate enzymes and substrates to study the impact of molecular confinement on the kinetics of enzymatic reactions [3]. First we shall discuss the impact of special confinement and vesicle size on enzyme kinetics using polystyrene-block-poly(acrylic acid) (PS-b-PAA) block copolymer (BCP) vesicles. We briefly review some of the fluorescence microscopy techniques to study single molecule behavior and demonstrate their applications in studies of single molecule enzymology [3]. We conclude that for several enzyme-substrate systems we studied the enzymatic efficiency increased with decreasing vesicle size by orders of magnitude [4].

BCP vesicles, often referred to as “polymersomes”, have been popular due to their simple preparation procedure and their unique structure which enables one to obtain both hydrophilic (interior/exterior) and hydrophobic (membrane) environments in a single particle. These systems need to be properly characterized, including the vesicle wall morphology, vesicle size and size distribution, vesicle wall modulus [4,5], and vesicle wall permeability. In this presentation we introduce and discuss these vesicle parameters and show options for their characterization. We then elaborate on various ways of encapsulating and releasing molecular cargos by these vesicles [6]. Considering release systems, particularly important is the responsiveness of the elastic properties resulting from variations in the solution environment when one of the BCP blocks is stimulus responsive. However, single container elastic properties are difficult to assess experimentally due to their sub-micron size. In the last example, we demonstrate how AFM based nano-indentation experiments can be used to address this issue [7].

References


TD-NMR Investigation of Nanoconfined Soft Phases in SEBS.

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Polymer chain dynamics can be investigated effectively by Time-Domain NMR (TD-NMR). The application of advanced pulse sequences based on excitation of multiple-quantum coherences provides rich information on polymer chain dynamics even with moderate technical requirements (e.g. low magnetic field). Multiple quantum coherences are physically enabled by the presence of residual dipolar couplings (RDC) caused by anisotropy of the long timescale dynamics of the polymer. Measurement of the RDC is then connected to physically relevant quantities such as entanglement or crosslink density, providing a powerful tool for the characterization of vulcanized and filled rubbers, polymer melts, gels, tethered and grafted polymers and other systems where constrained macromolecules are present. In this work we address directly the mobility of soft ethylene-butene phases confined by glassy polystyrene (PS) blocks. We studied samples of polystyrene-block-poly(ethylene-co-bu-l-ene)-block-polystyrene triblock copolymers (SEBS) with 20 and 65% (mol) butene content in the midblock. Samples were cast from toluene, letting polymer organize in the lamellar morphology [1]. TEM and SAXS confirmed a lamellar structure, with alternating PS and EB blocks with few nanometers thickness. All TD-NMR experiments were performed on a Bruker Minispec mq20. DSC was performed with a Mettler-Toledo calorimeter, at 10 K/min.

DSC analysis (Fig. 1) showed a broad endothermic transition in the sample with 20% butene (SEBS_L) upon heating from 221K to 300K. The transition was absent in the high butene copolymer (SEBS_H) that displays only a T_g at around 230K. This peculiar transition was observed in literature [2] and attributed, on the basis of indirect evidence, to a complex pseudo crystalline rearrangement of the mobile phase starting immediately above the glass transition.

Figure 1: Comparison of thermal analysis of the copolymer samples. SEBS_H and SEBS_L contain High and Low percentage of butyl respectively.
Between 230 and 370K, the PS layers are below $T_g$ and have a distinctively short $T_2$ while EB phase is comparatively softer, and can be investigated in depth by MQ experiments. Double quantum coherence intensity (DQ) of the mobile phase alone is normalized against a reference curve [3] and plotted versus excitation time in Fig. 2. The resulting dataset was fitted as a sum of contributions from protons with different residual dipolar coupling ($D_{res}$). Tichonov regularization procedure provides a distribution of $D_{res}$ without any preliminary assumption on its functional form.

![Figure 2: (left) best fitting of the normalized DQ intensity. (right) RDC distribution at 353K for the two samples.](image)

Distributions of dipolar couplings are plotted in the rightmost part of Fig. 2. In SEBS_H the $D_{res}$ are rather disperse but centred around a single value. SEBS_L instead has a bimodal distribution. Because of the extremely high number of butyl side chains in the SEBS_H, the mobile phase is fully amorphous. SEBS_L, while having a number of bulky side groups that is too large for proper crystallization, exhibits areas of increased order that are compatible with a rotator phase that could be visualized as a local concentration of interacting polyethylene like stems without the presence of butyl groups, which is statistically impossible in the case of SEBS_H that has about 1 butyl group every 4 repeating units. This behaviour, reminiscent of EP copolymer rotator phase, is recorded directly for the first time and is probably made possible by tethering of the EB chains on both sides to PS blocks and by the resulting confinement.

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**References:**


Analysis of Multi-Component Polymer Blends with the Confocal Raman AFM

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The characterization of heterogeneous systems on the microscopic scale continues to grow in importance and to impact key applications in the fields of materials science and nanotechnology. The development of advanced polymeric materials for applications such as these requires detailed information about the physical and chemical properties of these materials on the nanometer scale. However, some details about the phase-separation process in polymers are difficult to study with conventional characterization techniques due to the inability of these methods to chemically differentiate materials with high spatial resolution and without damage, staining or preferential solvent washing. Atomic Force Microscopy (AFM) has been used successfully for the characterization of heterogeneity in polymers. This method can provide spatial information along and perpendicular to the surface of a polymer film with resolution on the order of 1 nm. The differentiation of polymeric components using AFM, however, is only possible if the materials have different mechanical properties and reveal a contrast in phase images. On the other hand, confocal Raman microscopy, a technique which combines chemically sensitive Raman spectroscopy with confocal microscopy, reveals unique information about the distribution of chemical species in polymer blends from sample volumes smaller than 0.02 µm³.

Fig. 1: Raman spectra evaluated from the 2D spectral array by using advanced software tools (left) and color coded Raman image of a three component polymer blend (right).
In Raman spectral imaging mode, samples are imaged by acquiring complete Raman spectra in every image pixel, leading to 2D arrays of Raman spectra. These arrays are analyzed using advanced data analysis features such as cluster analysis and graph demixer followed by a basis analysis of the acquired data. In the cluster analysis the software automatically identifies similar spectra and classifies them in a used defined number of clusters. To determine the pure Raman spectra of the components, the graph demixer function was applied to the recorded array of spectra. With this function a weighted subtraction of spectra is performed. These unique Raman spectra are then used to determine the distribution of the evaluated components on the sample. Fig. 1 shows the unique Raman spectra of PS, EHA and SBR evaluated from a Raman spectral image data set acquired from a thin film of PS-EHA-SBR spin coated on a glass substrate. The distribution of the three components on the sample is shown as color coded Raman image.
FTIR Step Scan Photoacoustic Spectroscopy applied to the study of micro and nanostructures in Fluorinated Polymers

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Fluorinated polymers constitute a class of high performances materials, due to their outstanding properties like high thermal stability, chemical stability etc. They are generally utilized where demanding high tech applications are required; sometimes specific additives are mixed to polymer matrix in order to meet mechanical requirements, or inorganic fillers to get suitable hardness. In these cases, analytical tools suitable to reveal the different components and the capability to understand how they mix themselves one into other are needed. Another key point is the capability to obtain such information on the final form of the product, such as for example sample slabs or coatings on metal surfaces. In this respect it is a clear analytical advantage the capability to analyse the samples without any kind of preparation or mechanical separation (like cutting, sectioning).

Some particular techniques used in the vibrational spectroscopy are especially suitable for such purposes, and Photoacoustic spectroscopy is one of these technique [1,2]. Photoacoustic spectroscopy (PAS) has been used in order to study the additive distribution in an ECTFE (Ethylene-Chlorotrifluoroethylene) copolymer matrix [3], and to estimate the relative distribution of a PVDF (polyvinylidene fluoride) based matrix and inorganic fillers.

Different approaches have been used in the study of additive distribution, combining information obtained by optical spectroscopy to derive a rough estimation of additive particles size (it resulted to be in the order of $10^2$ nm) and using reflection and photoacoustic spectroscopy. Especially powerful resulted to be the step scan approach, that allowed us to do a depth profile analysis without any kind of sample manipulation, just changing experimental set up and the corresponding acquisition parameters [4,5]. The key parameter used to understand relative distribution has been the phase values of PAS signals of two bands, due to the additive and to the polymer matrix respectively (fig.1).

Interesting and fruitful information have been obtained during the study of a set of different coatings based on pvdf polymeric matrixes, using linear scan PAS spectroscopy.
Fig.1 Left side: Step scan Photoacoustic experiment (100 Hz Phase modulation). ECTFE polymer matrix containing 7% w/w plasticizer. Right side: Phase behaviour relative to plasticizer band at 1740 cm⁻¹, due to carbonyl ester group (up) and 1450 cm⁻¹ due to scissoring of CH₂ groups of polymer matrix (bottom).

References
Nanoscale Chemical Spectroscopy with the Atomic Force Microscope

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The ability to unambiguously identify arbitrary material under the tip of an Atomic Force Microscope (AFM) has been identified as one of the "Holy Grails" of probe microscopy. While the AFM has the ability to measure a range of material properties including mechanical, electrical, magnetic and thermal, the technique has lacked the robust ability to characterize and identify unknown materials. Infrared spectroscopy is a benchmark technique routinely used in a broad range of sciences to characterize and identify materials on the basis of specific vibrational resonances of chemical bonds. Several AFM probe-based techniques have been used to beat the diffraction limit of conventional IR measurements, however, none of these techniques provide readily interpretable broadband IR spectroscopy with nanoscale resolution. We have successfully integrated the capabilities of AFM with IR spectroscopy to allow chemical characterization on the micro and nanoscale. The instrument employs a technique called photothermal induced resonance (PTIR) [1-3] that uses an AFM probe to measure the local thermal expansion from IR light incident upon a sample. This technique enables the ability to obtain a high quality IR spectrum at a selected point in an AFM image and/or automatically map spectra at an array of points on a sample to enable chemical mapping. In this presentation, we will share the details of the measurement technique including application examples on polymer multilayers and blends, along with measurements on plant cells.
Figure 1. (L) Schematic diagram of PTIR technique for nanoscale IR spectroscopy. A pulse of infrared light from a tunable source is directed at a region on a sample. When the source is tuned to an absorption band of the sample, the absorbed radiation heats up the area, resulting in a rapid thermal expansion of the sample. This rapid thermal expansion excites resonant oscillation modes of the cantilever. (R) Example cantilever ringdown after excitation by sample IR absorption. The amplitude of this ringdown is proportional to the strength of IR absorption under the AFM tip. The PTIR technique also enables complementary and simultaneous mapping of mechanical properties through measurements of the ringdown resonant frequencies.

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References
Microindentation Study on Polypropylene/Cycloolefin Copolymer Blends

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*Corresponding author's Email: gzamfirova@mail.bg; Tel: +359 2 9709452; Heterogeneous blends based on polypropylene (PP) and cycloolefin copolymer (COC) were found to exhibit an interesting mechanical behavior [1] directly dependent on the fibrous structure developed during injection moulding process[2]. For this reason this investigation was devoted to a deeper evaluation of micro-mechanical behavior by means of microindentation study of both ISO-527 (210x12.8x3.3mm) and ASTM-D 638 (170x10x4mm) dumbbell specimens. Measurements include determination of:
- Vickers microhardness (MHV=kP/d², where P is the applied load, d is the mean diagonal length of the indentation after removing the indenter and k is a constant characterizing the indenter geometry);
- Total microhardness [3](MHT=kP/D², where D is the diagonal of the indentation in the loaded state);
- Mayers lines, which are a logarithmic form of the dependence between indentation diagonal and applied load (P = ad^n, where a and n are material constants);
- Microhardness profiles (MHV=f (h); MHT=f (h) where h is the indentation depth);
- Vicat test at 100MPa (VST and profiles p(T) where p is the penetration depth up to 1mm).

MHV and MHT were measured for all composition at applied load of 80g. Microhardness profiles were obtained for pure polymers as well as for the compositions PP/COC: 85/15, 50/50 and 25/75.

Fig. 1 shows experimental MHV and MHT results for ISO 527 and ASTM D638 samples. It is evident the deviation from linearity (dashed line) for both type of specimens in agreement with microstructure. Moreover, the inherent i-MHV and i-MHT of PP and COC in the blends were determined applying the additive rule [4] for a two component system. The calculated MHV values for both components are
presented in Fig. 2. Vickers microhardness i-MHV of the COC component passes through a maximum (215-220MPa) at about 0,15 COC volume fraction, due to the amorphous fibrous structure [2].

On the other hand, i-MHV value of PP component remains almost constant at about 100MPa up to 0,20 COC volume fraction, and then rapidly decreases. Another approach for determination of the inherent microhardness values of COC component is by extrapolating of the initial linear part of the both dependencies in the Fig.1 at 100% of COC, showing a good correlation with previous data.

![Graph 1](image1)

![Graph 2](image2)

Fig.2

Vicat Softening Temperature (at 100MPa, 2°C/min) was found to progressively increase from 69°C (PP), to 72, 83, and 87°C for 75/25, 50/50 blends and COC respectively, confirming the stiffening role of COC. An interesting correlation between Vicat and MHV penetration profile was also observed.

**Conclusions:**
- Microhardness measurements confirm the marked reinforcing role of the COC fibrous component up to about 0,25 volume fraction; at higher COC content i-MHV of PP decreases, and its contribution to the MHV of the blends becomes further negligible.
- The imprint appearance was found to change with composition. The surface layer is formed by PP for all blend compositions. The elasticity of the blends and its PP component decrease with COC content, and correspondently their rigidity and fragility increase, while the COC fibres elasticity decreases when fibre diameter becomes smaller.
- Two reliable methods for determining the inherent microhardness parameters of the blends components (additive law and extrapolation) were successfully applied.
- Vicat experiments at high static stress (VST and penetration profile) were found in good correlation with MHV data of various blends.

**Acknowledgements**

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Posters
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3. Improved in SEC-FTIR method for the characterisation of multimodal HDPE
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Epoxy/Multiwall Carbon Nanotubes Composites Evaluated by Microindentation

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Epoxy/multiwall carbon nanotubes composites were the object of the investigation performed by different microindentation methods. The samples within the concentration range from 0 to 1.0 wt% carbon nanotubes were prepared from OLMA by two different processing modes: with functionalization and without functionalization of the filler. Polyethylene polyamine (PEPA) was used as a curing agent.

The following microhardness characteristics were measured at room temperature on a dynamic ultra microhardness tester DUH-211S:

- The Vickers microhardness (MHV) was determined on the basis of the diagonal length of the square imprint (d) after removing the indenter. This characteristic is connected with the irreversible component of deformation and gives information about the plastic properties of the sample.

\[ MHV = \frac{kP}{d^2}, \]

where (P) is the applied load and (k) is a constant depending on the geometry of the pyramid.

- Dynamic hardness (DH):

\[ DH = \frac{aP}{h^2}, \]

where (a) is a constant which depends on the shape of the indenter and (h) is a indentation depth. This characteristic reveals the material’s strength against to plastic, elastic and viscoelastic deformation components of the sample.

The other microindentation characteristics were determined on the basis of the relationship between the test force and indentation depth measured by a load-unloading test during the indentation process in accordance with ISO 14577-1 standard. The test provided the following characteristics:

- Martens harness (HM) was determined from the slope (m) of the increasing force/indentation depth curve in the 50% ÷ 90% P interval:

\[ HMs = \frac{1}{26.43m^2} \]
-Indentation hardness (Hit) according to the model of Oliver-Pharr [1] is a measure for the resistance to permanent deformation.

\[ \text{Hit} = \frac{P}{24.5 \times h_c^2} \]

where \(h_c\) is the depth of contact of the indenter with the test piece.

The samples prepared by the two modes had different microindentation behavior. The samples without preliminarily functionalized nanoparticles showed a decrease of the microhardness parameters at small MWCNTs content (Fig. 1a), while the functionalized ones exhibited an increase in all measured microhardness characteristics at a very small filler content (about 0.03wt.%) due to better exfoliation (Fig. 1b). However, an additional portion of MWCNTs causes again a diminishing of their hardness.

Microhardness profiles were obtained from the indentation curves. They allowed the estimation of the level of the materials homogeneity, which as expected was better for the preliminarily functionalized carbon nanotubes. The indentation module of elasticity was also determined. SEM images present the structure of some samples.

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**References:**

Possibilities of Quantification of Polymer Long-Chain Random Branching by SEC with Light-Scattering and Viscosity Detections

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Branching of macromolecules affects substantially the properties of polymers, including their material and serviceable properties. Studies on branching of macromolecules, long-chain branching in particular, are a topical issue of the present-day polymer science. The most important characteristics of branching are the contraction factors (branching indices) $g$ and $g'$. The first is the ratio of the radii of gyration, $g = \langle s^2 \rangle_b / \langle s^2 \rangle_l$, the second of intrinsic viscosities $g' = [\eta]_b / [\eta]_l$, of branched polymers and polymers with linear chains of the same molecular weight, $M$, and (almost) the same chemical composition (subscripts ‘b’ and ‘l’, respectively). For polystyrene, the ratios can be obtained by knowing the molecular weight by use of literature relations between molecular weight and intrinsic viscosities and radii of gyration for linear-chain polymers, e.g., Refs. [2-3]. One of the important classes of long-chain branched polymers are randomly branched polymers formed by cross-linking of linear polymers. Copolymers of styrene and divinylbenzene in small quantities are a suitable model system. The latter monomer forms in the branched molecule tetrafunctional branch-points. Detailed description of branched polymers is extremely difficult because the individual molecules differ not only in molecular weight, as linear homopolymers, but also by number of branch points, and molecules with the same molecular weight and number of branch points differ by positions of branch points within the molecule, i.e., by topology. The understanding of random branching and its mathematical background are still insufficient and requires further investigation. For gaining insight into the branching mechanism and its influence on molecular size and molecular weight, we undertook a study on solution properties of copolymers of styrene with a small amount of divinylbenzene randomly branched to various degrees.

Fig. 1. Refractive-index (RI) elution curve and output of the SEC characterization of a styrene-divinylbenzene copolymer, $M_w = 9.69 \times 10^4$, $M_w/M_n = 3.61$. The preparation of samples is described elsewhere [1]. The samples were analyzed by size exclusion chromatography (SEC) equipped with the multiangle light scattering (DAWN-DSP-F, Wyatt Technologies, Ltd.), viscometric (TriSEC, Viscotek) and concentration detectors. Tetrahydrofuran was the mobile phase. The triple detection makes it possible to characterize the polymer material eluted from the SEC separation system by molecular weight, radius of gyration and intrinsic viscosity (Fig. 1). Using the experimental data from Ref. [1], we constructed the dependences of molecular weights, radii of gyration and intrinsic viscosity on elution volume. It can be seen that the dependences depicted in Fig. 1 are practically linear in a broad range of elution volume. This made possible to draw lines through the dependences and thus to combine them in any point of elution volume. We obtained the contraction factors (branching indices) in a large scale of elution volume. However, the data from the marginal parts of the elution curve, especially from the low-$M$ shoulder, were highly scattered. We therefore used only the central points of each dependence, close to the maximum of the elution curve, to deduct the $g$ and $g'$ values.
The dependences of $g$ as well as $g'$ on reduced molecular weight, $M_{\text{red}}$, are a measure of topological similarity of branched structures with the same number of branch points but differing in molecular weight [4]. The quantity $M_{\text{red}}$ was obtained by a division of the actual molecular weight by that of primary chains. The molecular weight of the primary chains was estimated from molecular weights of samples of linear-chain polymers, taken from the polymerization mixture in the beginning of the polymerization where, as we believe, the branching process has not started yet or has not progressed to a noticeable degree. The reduction of molecular weight to $M_{\text{red}}$ considerably decreased the scatter of the data points in comparison with plotting $g$ and $g'$ against $M$.

The dependences of $g$ as well as of $g'$ plotted vs $M_{\text{red}}$ (Fig 2) form in a semilogarithmic plot quasilinear master curves suggesting topological similarity of molecules with equal $M_{\text{red}}$ values.

Fig. 2. Dependence of $g$ and $g'$ on reduced molecular weight, $M_{\text{red}}$, for copolymers of styrene with a small amount of divinylbenzene.

Although the data are aggravated by errors, coming from the fact that the conditions of preparation of samples differed, as well as from the difficulties to set a linear dependence through the experimental dependences in Fig. 1, linear lines can be drawn through the experimental points in semilogarithmic plots of $g$ and $g'$ vs $M_{\text{red}}$.

From Fig. 2, it can be seen that the slope of $g'$ vs $M_{\text{red}}$ is higher then that of the dependence of $g$ vs $M_{\text{red}}$. This brings the question of the relation between the branching indices $g$ and $g'$.

Fig. 3. The dependence of branching indices $g$ vs $g'$, for copolymers of styrene and divinylbenzene

For the dependence of $g'$ vs $g$ in double logarithmic plot, we obtained $g' = g^{0.71}$ (Fig. 3). This result gives us the possibility to obtain from values of $g'$ the values of $g$, the latter being related with the average number of branch points $m$, on the basis of the Zimm-Stockmayer theory by the well-known formula [5]

$$g(m) = [(1 + m/6)^{1/2} + 4m/3\pi]^{-1/2}$$

To characterize randomly branched samples by determining the branching density, it is necessary to solve this equation numerically for $m$ to obtain thus the branching density. One has to keep in mind that the values thus obtained are only average and approximate.

References
P3

Improved in SEC-FTIR method for the characterisation of multimodal HDPE

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The determination of the chemical heterogeneity of synthetic polymers is crucial for understanding structure-property relationships, polymerization mechanisms and kinetics, and polymer reaction engineering. By the usage of different separation techniques the polymer can be fractionated regarding different specific characteristics of their microstructures e.g. molecular weight, chemical composition, comonomer sequence length, tacticity, and long-chain branching.\textsuperscript{1} To obtain a full profile of the chemical heterogeneity (molecular weight distribution along the chemical composition distribution or vice versa) cross fractionation techniques can be applied. These techniques e.g. temperature rising elution fractionation coupled with size exclusion chromatography (SEC)\textsuperscript{2}, two-dimensional high performance liquid chromatography (2D-HPLC)\textsuperscript{3,4} or a preparative fractionation\textsuperscript{5} followed by SEC and nuclear magnetic resonance (NMR) spectroscopy are either time-consuming\textsuperscript{2} or the interpretation of the results are challenging but sometimes valuable.\textsuperscript{2,4}

The use of hyphenated techniques like size exclusion chromatography couple to Fourier transform infrared spectroscopy (SEC-FTIR)\textsuperscript{6,7}, SEC-IR (composition detector)\textsuperscript{8} can be quite a good practical solution for the elaboration of a deeper understanding of material properties in polyolefin research and product development.

In this work a developed SEC-FTIR method for the analysis of high density polyethylene copolymers having superior resolution for the determination of short chain branching as a function of time and improved repeatability by hardware adaptation and processing optimisation is presented.

The signal to noise ratio at the IR detector could be increased significantly and influences of system instabilities could be decreased by changes in data processing.
Due to this adaptations reliable short chain branching information especially in the flanks of the high molecular weight region for multimodal HDPE samples in respect to accuracy and repeatability with better chromatographic resolution could be achieved.

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Synthesis and Characterization of Novel Derivatives from Vegetable Oils

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As part of our interest in utilizing vegetable oils as cheap and bio-renewable raw materials, we have found derivatization reactions, particularly with nitrogen-containing reagents, to be good pathways to achieve a range of new vegetable oil-based products. In this presentation an overview is given of our efforts in this area. One of our approaches is to derivatize epoxidized soybean oil and methyl epoxy soyate through environmentally friendly reactions. Thus, amination reactions are relatively easy to carry out and provide several examples of interesting products. The click reaction is another example whereby new vegetable oil-based materials can be made through the reaction of an azide and phenylacetylene. These structural modifications are tools that permit specific molecular groups to be attached to vegetable oils or their methyl esters in order to improve specific properties. With suitable modifications, it may be possible to produce vegetable oil-based materials with potential applications in lubrication, heat resistance, uv protection, drug encapsulation, and surfactancy. The materials generated in this work have been fully characterized by NMR.
Latex gloves are quite frequently employed by felons who want to avoid shedding fingerprints or biological traces. Less forensic aware crime committers, though, may discard the gloves at the crime scene or nearby. If found and properly analyzed, these items may therefore provide useful information to investigators. Today’s industrially produced gloves are mostly based on polyisoprene, but may be based on other elastomers. They also contain several kinds of additives like dyes and antioxidants as well as inorganic fillers to regulate mechanical properties and make up bulk inexpensively. Thus, latex gloves display a compositional variability that can depend on the type, producer and batch, allowing to perform a meaningful differentiation from the forensic point of view.

**Figure 1**: a) Calibration Curve relating compounds of known H content with experimental weight-normalized NMR signal intensity b) Gloves from different producers and batches, represented on a 2D plot of the different quantities measured by NMR.

We propose the use of proton time domain nuclear magnetic resonance ($^1$H TD-NMR) as a method of forensic characterization of latex gloves. TD-NMR has recently become a very important tool for the characterization of vulcanized and filled elastomers and rubber materials. [1] Two parameters were quantified by this technique: the Hydrogen weight fraction H, which is correlated to the chemical
nature and formulation of the material which composes the gloves, and the relaxation time $T_2$, which is a measure of chain mobility, and is thus dependent on the proximity to glass transition, presence of entanglements and degree of crosslinking of the macromolecular chains.

The hydrogen weight fraction is calculated from the ratio of absolute signal intensity at fixed temperature after a 90° pulse against the mass of the sample. In order to attain independence from instrumental parameters, a calibration line [2] was constructed in the 2% to 15% range using several widely available reference samples of known proton weight fraction like toluene and xylene as well as commercially available reference polymers. The calibration line is shown in Fig 1a. Transverse proton relaxation times were instead measured using the well established CPMG pulse sequence. Both measurements showed an high degree of repeatability over a time of several months. The complementarily of the data and the discriminating power of the technique are highlighted by positioning all the data points in 2D plot of the two variables, as seen in Fig. 1b, where it is immediately seen that the data are not correlated.

The precision of the technique was thoroughly analyzed, considering not only the usual sources of error but also the variability between samples from the same box. In fact, for forensic purposes, it is not sufficient to establish the precision and repeatability of the single measurement. It is also necessary to ensure the intrabox variability is small enough to consistently connect the items found on the crime scene with the rest of the box.

By this very straightforward and inexpensive technique, without sample preparation, more than 85% of the possible pairs of samples in a population of 21 commercial latex gloves were differentiated even considering the intrabox error.

A comparison with established techniques like TGA-DSC [3] was performed in terms of Principal Component Analysis. TGA-DSC characterize the complex thermal degradation phenomena, with observables such as weight loss or decomposition enthalpy. There is some correlation between proton content of the sample and parameters of the degradation. This was not unexpected since the presence of H strongly correlates to chemical structure of the sample. On the other side, the $T_2$ values that are intrinsically semi-local and relative to the behaviour of the chain as a whole, were much less correlated, providing a fresh point of view on the material. Therefore, TD-NMR can be integrated with established thermal analysis characterization within a thorough forensic characterization protocol, with the additional advantage of non-destructivity.

The rather large degree of variability existing in latex gloves, even though they are mass produced, was shown, confirming the usefulness of comparisons between items related to the crime scene and those seized in the suspect’s premises.

References:

Determination of Comonomer Sequence Distributions in Methacrylate Terpolymers by Multivariate Analysis of 13C NMR Spectra

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NMR spectroscopy is widely used for molecular characterization of polymers. However, NMR spectra of multi-component copolymers often show complicated splitting due to comonomer sequences and configurational sequences, and thus direct analysis of those spectra is troublesome. Recently, we applied methods of multivariate analysis to the analysis of 13C NMR spectra of methacrylate copolymers to extract quantitative information about chemical composition and comonomer sequence distribution of the copolymers\cite{1,2}. In the present paper, we focused to the analysis of comonomer sequence distributions in the terpolymers comprising of methyl methacrylate (MMA), tert-butyl methacrylate (TBMA) and 2-hydroxyethyl methacrylate (HEMA) [poly(MMA-co-TBMA-co-HEMA)s].

All homopolymers, copolymers, and terpolymers used in this study were prepared by polymerization with 2,2'-azobisisobutyronitrile (AIBN) in ethyl lactate at 80 °C under a nitrogen atmosphere. 1H and 13C NMR spectra were measured for 8 % (w/v) solution in a 4/6 (mol/mol) mixture of CDCl3 and DMSO-d6 at 55 °C using a JEOL ECX-400 spectrometer equipped with a 10 mm 13C-15N{1H} tunable probe. An Alice2 ver.5 for metabolome ver.1.6 software (JEOL) and a Sirius ver.7.0 software (Pattern Recognition Systems) were used for the principal component analysis (PCA) and partial least-squares regression (PLSR) of the data sets. Bucket integration of the spectral regions 13.0–21.0 ppm (the $\alpha$-methyl carbons), 41.5–45.5 ppm (the backbone quaternary carbons) and 173.0–177.0 ppm (the carbonyl carbons) was performed at an interval of 0.05 ppm.

Figure 1 shows PCA score plots for the data set of the integral intensity of 113 samples (3 homopolymers, 34 blends of the homopolymers, 16 poly(MMA-co-TBMA)s, 14 poly(TBMA-co-HEMA)s, 14 poly(MMA-co-HEMA)s, and 32 terpolymers). The variances for the first (PC1), second (PC2) and third principal components (PC3) were 45.6, 27.0, and 14.6 %, respectively, and their total amounted to 87.2 %, indicating that the spectral information of the data set was explained well with these three components. Three-dimensional PCA score plots for the data set distributed in a triangular pyramid zone. The plots for the three homopolymers and their blends were distributed on its bottom plane nearly parallel to the PC1-PC2 plane as a ternary diagram. The PC1 and PC2 score mainly
reflected the chemical composition of the samples[2,4]. The plots for the copolymers of three systems were distributed on each side surface on the pyramid zone, and those for the terpolymers were distributed inside of the zone. The plot for the equimolar chemical composition of co- and terpolymers were located on the top of the zone, along PC3 axis. These results suggest that the PC3 score should reflect heterogeneity of comonomer sequences in a manner similar to the PC2 scores in the poly(MMA-co-TBMA)s system.

As an index of heterogeneity of comonomer sequences in the terpolymers, the summation of the fraction of three hetero dyad sequences (fMT; MMA-TBMA, fTH; TBMA-HEMA, and fHM; HEMA-MMA), f2-hetero was employed. Linear relationship between the PC3 score and the f2-hetero of terpolymers was obtained with a correlation coefficient (R2) of 0.930. Figure 2 shows the correlation between the f2-hetero calculated from the monomer reactivity ratios and the chemical compositions of terpolymers, and the f2-hetero predicted by PLSR using the three homopolymers and 15 terpolymers obtained at early stages of polymerization as a training set. A linear relationship with a relative standard deviation (RSD) of 9.1% and an R2 of 0.975 was obtained.

References
Viscoelastic Characterization of Poly(methacrylate)s

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Poly(methacrylate)s are a very well known family of vinyl polymers which can be obtained with a broad variety of organic and inorganic substituents. This is an important aspect from viscoelastic point of view, because it is possible to obtain a great variety of polymers with small differences in their chemical structures and therefore to study the effect of the side chain structure on the viscoelastic responses of these kind of materials. The comparison of the viscoelastic responses is a powerful tool to know the origin of the molecular motions responsible of the fast relaxations processes that take place when the material is submitted to different field forces [1]. Small differences in the chemical structures allow to know the influence of the fine structure on the response of polymer chains to perturbation fields. The effect of the side chain can be studied taken different types of substituents. In this work the dynamomechanical behavior of poly(methacrylate)s can be splitted among those containing aliphatic, saturated cyclic rings and aromatic substituents.

A comparative study of the response of poly(dimethoxy benzyl methacrylate)s to electrical perturbation fields over wide frequency and temperature is investigated in order to know the influence of the location of the dimethoxy substituents in the phenyl moieties on the relaxation behavior of the polymers. The dielectric loss isotherms above Tg exhibit a blurred relaxation resulting from the overlapping of secondary relaxations with the glass-rubber or glass-rubber relaxation [2]. At high temperatures and low frequencies, the glass transition can be detected, associated to the glass-rubber relaxation.

Poly(2-chloroethyl methacrylate) (P2CEM) and poly(3-chloropropyl methacrylate) (P3CPM) are aliphatic substituted polymers which show important conductive and dipolar components in the dielectric spectrum [1]. Three relaxation phenomena are observed from dielectric and viscoelastic spectra. At high temperature and the glass transition can be detected,
which is partially covered in the dielectric experiments by the increase of dielectric loss $\varepsilon''$ at high temperature attributed to conduction process. $\beta$ and $\gamma$ processes are also observed.

Polymers containing cyclic saturated side chains is another very interesting family of polymers from dielectric and dynamomechanical point of view. These polymers show several relaxation processes due to the conformational versatility and because they are able to present several conformational states. The chains have a large number of degrees of freedom which can produce several molecular motions. This structural fact, produces a great variety of transitions and relaxations when the material is affected by mechanical or dielectric force fields. Moreover, the flexibility of the saturated rings also allows to flipping-chair-to-chair–motions of the cyclohexyl group [3]. These motions have been attributed as the responsible of the molecular origin that produce rapid relaxation processes in dynamic mechanical as well as dielectric measurements. The important subglass absorption exhibited by the mechanical spectra of polymers with cyclohexyl groups is produced by flipping motions of the ring. A mechanism of this type is also suggested to explain the subglass absorption appearing in the dielectric relaxation spectrum of substituted poly(methacrylate)s [1,5]. The most simple poly(methacrylate) containing saturated cyclic side chain is poly(cyclohexyl methacrylate) (PCHM) which dielectric and mechanical behavior have been described by Díaz-Calleja et al. [6]. PCHM shows a variety of absorptions due to the versatility of its structural moiety. The effect of the flexible spacer groups on the dynamic mechanical and dielectric behavior of polymers have been taken into account in order to gain confidence about the molecular origin of the relaxations in this

References


Fluoro-Functionalized PLA-Polymers as Potential Water Repellent Coating Material for Protection of Stone

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The work involves the synthesis and characterization of polymers coming from renewable sources and their evaluation for protection of porous materials.

A series of sixteen fluoro-functionalized PLA polymers were synthesised using two commercial fluorinated alcohols [3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroocetyl)benzyl alcohol] as co-initiators in the ring-opening polymerization of L-lactide and rac-lactide (the racemic mixture of L- and D- lactide) catalyzed by Sn(Oct)$_2$\cite{1}. The main feature of these polymers is their low fluorine content with respect to other polymers such as PLA-FLK-PLA block copolymers, which have been recently suggested as potential candidates for protective and surface modifier\cite{3}.

The polymers were fully characterized (by NMR, IR, GPC, DSC) and tested for coating purpose on selected stone substrates. The performances were evaluated by colorimetric analysis and water capillary absorption. Furthermore the photo-stability of nine selected polymers was investigated through accelerated ageing test using a Solar Box.

It has been shown that the presence of fluorine has a positive influence on the water-repellent effect. The polymers showed also interesting photo-stability properties and some of them proved a behaviour close to PLA-FLK-PLA block copolymers, in spite of their lower fluorine content. Nevertheless, it has to be noted that the new polymers lead to interesting advantages with respect to PLA-FLK-PLA i.e, higher solubility in traditional friendly organic solvents, higher eco-compatibility and cheapness. Nowadays the results obtained represent an important achievement for the protection of porous materials and an interesting alternative to conventional petrochemical-based products.

References


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Mesoporous titania films were synthesized by a soft templating method based on the use of organic/inorganic mixed micellar solutions consisting of PS-\(b\)-PEO copolymers as templates and sol-gel precursors for the \textit{in situ} growth of mesoporous TiO\(_2\) [1]. Thin hybrid PS-\(b\)-PEO/TiO\(_2\) films were prepared by casting or spin coating the micellar solutions. After formation of an extended inorganic network by condensation of the sol-gel precursor the organic template was removed by thermal degradation to give the solid negative replica of the original micellar system.

A variety of morphologies were obtained by tuning molecular (i.e. size of each copolymer block, overall molecular weight) and solution parameters (i.e. solvent/non-solvent ratio, types of solvents, copolymer concentration, presence of additives) [2]. In general, block copolymers which self-assembles in domains 10-30 nm sized were selected, that is with dimensional characteristics suitable for the design of photonic and photovoltaic devices, as well as for possible applications as photocatalytic or conductive materials. For the same reason the inorganic content was varied in a wide range of compositions, with a special focus on micellar systems with PS cores and PEO/TiO\(_2\) coronas giving nanostructured hybrids with strongly interconnected inorganic domains. Moreover, the reduced dimensions of TiO\(_2\) nanocrystals and nanostructures made possible to achieve enhancement in the structural and surface properties of the material, such as superhydrophylicity.

Degradation of the polymer template and simultaneous crystallization of TiO\(_2\) was achieved by thermal treatments. Following this approach to synthesize nanostructured oxides, the main difficulty is the stability of the inorganic network upon removal of the template. The problem is that titania has a rather low nucleation-to-growth rate and when operating at high temperature an excessive crystallization and grain growth of the inorganic phase may result in too big nanoparticles [3]. Thus a
study was carried out in order to find the best experimental conditions able to remove the polymer template without collapsing the mesoporous structure.

Various techniques were applied to characterize the final mesoporous titania films: powder X rays diffraction (XRD) analysis, to determine the structural modifications induced by the preparation steps and the possible presence of undesired crystalline products; gas-volumetric N₂ adsorption at 77K, to determine specific surface area and porosity; atomic force microscopy (AFM), to monitor the surface morphologies of both hybrid films and titania nanostructures; electrostatic force microscopy (EFM), to measure the charge distribution of the sample surface; contact angle measurements, to evaluate surface hydrophilicity/hydrophobicity.

References


Characterization of polysaccharides with Thermally Assisted Hydrolysis and Methylation

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In the present work polysaccharide materials used in the field of cultural heritage where characterized. Standard monosaccharides, disaccharides and polysaccharides were analyzed to understand which are the characteristic compound formed in the Thermally Assisted Hydrolysis and methylation (THM) and useful for identification of these materials. Pyrolysis under strong alkaline conditions in the presence of methylating reagent (TMAH) was found to cause the formation of metasaccharinic and isosaccharinic acids, characteristics for each monosaccharide and differing according the types of glycosidic linkages. All the markers were identified on the basis of their mass spectra, characterized by the presence of the intense signal at m/z 129 [1].

Different conditions were varied to optimize the method: pyrolysis temperature, concentration of alkaline reagent and contact time between sample and reagent. The optimized method was applied to the study of plant gums, in particular gum Arabic, gum tragacanth, cherry gum, gum karaya and gum ghatti [2]. Principal monosaccharide markers were identified in the pyrograms of the gums and classification was obtained with chemometric data treatments. Not all the mass spectra of the compounds found in the ancient Egyptian cartonnage.
gums have been assigned. In particular four unknown peaks, very intense and considered to be indicative of the presence of polysaccharide in the sample, need to be assigned. Further studies on possible fragmentations pathway must be developed.

Effects of artificial accelerated ageing were also investigated. Gums were submitted to photooxidation, alone and in the presence of metallic pigments, and it was demonstrated that these polysaccharides are very stable to oxidative processes. Plant gums were also stable under mild thermoxidative conditions. Only enzymatic treatment and ozonolysis induced strong changes in the molecular components of the plant gums. In particular ozonolysis causes depolymerization and with the enzymatic treatment glucose, not present in the starting samples, was always produced. The mechanism that causes the formation of glucose is not presently known. The plant gums modifications induced by these treatments are considered too strong and substantially different from the natural ageing processes.

As example of application, samples from ancient Egyptian cartonnage were analyzed. In these samples traces of monosaccharide markers were found, allowing to prove the presence of a fruit tree gum. This case study confirms that THM coupled with chemometric data analysis is a suitable procedure to identify plant gums even in very low concentrations and with a minimum amount of sample, that is the principal aim of the present project.

References:

In the tire industry, synthetic styrene-butadiene rubber (SBR), butadiene rubber (BR), and isoprene rubber (IR) are essential elastomers for conferring on the product its mechanical and grip properties, mileage and rolling resistance.

The radical or anionic polymerization of diene monomers can generate different isomer units: 1,2-vinyl BR, 1,4-cis BR, and 1,4-trans BR, in the case of butadiene; and 3,4 IR, 1,2-vinyl IR, 1,4-cis IR, and 1,4-trans IR for isoprene. The relative amount of these units is called the microstructure of the polymer. In the case of SBR copolymers, which contain styrene units in addition to the three butadiene units, the polymer composition is also characterized by the styrene content. Several techniques are utilized for the quantification of the relative amount of the different units, among others the most used are high resolution nuclear magnetic resonance (HR-NMR) spectroscopy and infrared spectroscopy (IR). NMR, especially in the case of HR $^{13}$C experiments, can easily identify and quantify the different units [1,2]. However $^{13}$C NMR has the relevant limitation to be time consuming, limiting its use as analytic method in the industrial laboratories. Since $^{13}$C isotope is naturally present only at the level of 1.1%, $^{13}$C NMR is intrinsically a low sensibility technique compared for example to $^1$H NMR. In order to have good signal to noise ratio signal averaging is necessary and overnight measure is required. Practically, HR $^{13}$C experiments are performed on samples constituted by a polymer dissolved in a suitable solvent (usually deuterated CHCl$_3$). Concentration should be rather low in order to have low viscous solution; 10-20% w/v can be considered as limiting concentrations, so during the measurement less than 20% of the sample is really measured. Therefore the first thing to do, in order to increase the signal to noise, is to work with bulk samples without any solvent. This straightforward solution however presents several drawbacks, in fact in a solid, chemical shift anisotropy, dipolar couplings and magnetic-susceptibility-induced line broadenings can lead to very broad and featureless resonances. For this reason several solid state techniques have been developed during the last 50 years: Magic Angle Spinning (MAS) is probably one of the most efficient method for cancelling chemical shift anisotropy and magnetic-susceptibility-induced line broadenings. In this experiment the sample is spun in a rotor at 10-15 kHz around an axis which makes an angle of 54.77° with the axis of the magnet (the so called magic angle). However, considering BR, SBR and IR $^{13}$C MAS NMR, experiments can be problematical, in fact for elastomers high power proton decoupling, usually used in $^{13}$C MAS NMR spectra of crystalline systems in order to cancel the line broadening due to carbon proton dipolar coupling, does not work properly. A possible solution to this problem is to record
spectra at 100 °C. At High temperature however $^{13}$C $T_1$ relaxation times become longer causing a further lengthening of the measuring time, maintaining the sample at high temperature for long can also lead to chemical degradation. A reliable alternative can be the use of the technique called High Resolution MAS.

HR-MAS NMR spectroscopy is a powerful tool that allows the application of most high-resolution techniques, well known from solution-phase NMR spectroscopy, together with the spinning at the magic angle [3]. Practically the HR-MAS probe is a MAS probe with gradients and lock channel, where the MAS rotors have spacers that provide a sample volume approximately spherical in order to improve the shimming of the probe. Since the HR-MAS probe is build for liquids and gels the sample volume is sealed by a screw.

The method we propose is to analyze by HR-MAS rubber samples swollen with a suitable deuterated solvent, in such way that the solvent can provide the polymer chains enough mobility to produce narrow resonances similar to liquid state without increasing the temperature. Finally we demonstrate that also in a polymer gel the addition of paramagnetic metal complexes like chromium(III) trisacetylacetonate, Cr(acac)$_3$, can reduce drastically the $^{13}$C $T_1$ relaxation times without increasing the peak line-widths (Figure 1).

Figure 1. $^{13}$C HR-MAS spectrum of a vulcanized compound constituted by NR, BR and SBR (1:1:1 w/w) swollen by CDCl$_3$, spinning speed 5 kHz. CDCl$_3$ is omitted for clarity. Cr(Acac)$_3$ 50 mM is used as relaxation agent. Experimental time: 2 hours.

References

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Unusual Morphologies in Fluorinated and Sulfonated Block Copolymers

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Recently, we have been investigating the synthesis and bulk morphology behavior of model block copolymers derived from precursor poly(styrene)-b-poly(isoprene) (PS-b-PI), which was first fluorinated in the PI block (fPI) followed by partial sulfonation of the PS block (sPS) [1-4]. Due to its ionic nature (sulfonic acid/sodium salt, highly hydrophilic) and fluorine content (strongly hydrophobic, even lipophobic), a high value of the Flory-Huggins interaction parameter $\chi$ is expected, which leads to novel self-assembly behavior. For example, a diblock copolymer of 75 vol% fPI and 25 vol% sPS, where the PS block was 50% sulfonated to the sulfonic acid form, when cast from anhydrous tetrahydrofuran (THF) formed “inverse morphologies”. The minority blocks (sPS) formed the continuous phase, due to charge percolation, with dispersed hexagonally packed and well ordered cylinders of fPI. This is the inverse of the morphology exhibited for the precursor PS-b-PI of the same volume fractions, which is a continuous PI phase with dispersed PS cylinders. Thermal annealing or addition of water to the casting solvent disrupts the percolated charges and promotes aggregation of ionic sites leading to a disordered system.

We are now beginning to study the self-assembly behavior of such novel block copolymers in aqueous media. These polymers show unique self-assembly behavior, forming tapered rods and ribbon-like nano-structures, which have not been previously observed. It is believed that residing in the super-strongly segregated regime and a distribution of sulfonation degree drive the self-assembly of these materials in a unique way, accounting for interfacial flatness and axial dimensional changes. The spatial distribution of the sulfonation degree, and the asymmetry of the nano-structures, opens up a new approach to controlling self-assembly of block copolymers. The sulfonation degree strongly impacts the self-assembly of the polymers in THF, and the inversion of aggregates as water is gradually added potentially sheds light on application in cargo delivery.

References
Investigation on the Structure of Poly(Ethylene Terephthalate) Fibres

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The knowledge of structures of fibres is relevant either in quality control, in view of assessing their performances, or in forensic sciences for identification of exhibits. Attenuated Total Reflection Infrared spectroscopy (ATR) and Pyrolysis coupled to GC/MS (PY-GC/MS) are both powerful investigation tools which give evidence of the molecular structure and are able to make evident even small differences imputable to a different synthetic route. Both these techniques work well on very small amount of sample (about 1 mg).

A few samples of poly(ethylene terephthalate) fibres of different origin have been characterised by ATR and PY-GC/MS. Concerning PY-GC/MS, analyses have been carried out in quadruple both with and without on-line derivatisation using tetramethyl ammonium hydroxide (TMA) which leads to the formation of methyl esters/ethers in place of acids/alcohols: repeatability was found satisfactory once derivatisation conditions have been optimised.

ATR results shown in Fig. 1 reveal some differences in fibre 4.

Fig. 1 ATR of poly(ethylene terephthalate) fibres
Products evolved from Py-CG/MS have been identified however degradative pattern was highly simplified after derivatisation. In particular Fibre 4, showed the presence of isophthalic acid methyl ester alongside terephthalic acid methyl ester. This can be referable to the presence of isophthalic ester in the original fibre as it can occur in fibres from PET recycled from bottles. Diethylene glycol structure has also been highlighted in some samples, an irregularity which can be formed during the production of PET and that is indicative of the synthetic batch conditions.

Fig. 2 PY-GC/MS of two samples of poly(ethylene terephthalate) fibres. Derivatization with TMA

References
Configurational Analysis of Poly(methyl methacrylate-co-tert-butyl methacrylate)s by Multivariate Analysis of $^{13}$C NMR Spectra

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Many functional polymer materials are multi-component copolymers. Detailed analysis of their primary structures is necessary for improvement in material performances. NMR spectroscopy is one of the most powerful tools for their analysis of copolymers. However, resonances arising from each group in copolymers often exhibit superposed splitting due to comonomer sequences and configurational sequences, and thus assignment of the individual peaks is troublesome. Recently, we successfully determined the chemical compositions of methacrylate copolymers$^1$ and terpolymers$^2$ by multivariate analysis of $^{13}$C NMR spectra without assigning the individual resonance peaks. In the present paper, this approach was extended to obtain quantitative information about tacticity of poly(methyl methacrylate-co-tert-butyl methacrylate)s [poly(MMA-co-TBMA)s] prepared by radical copolymerization at –40 to 40 °C.

Twelve copolymer samples were prepared by polymerization with 2,2'-azobisisobutyronitrile (AIBN) in ethyl lactate at –40, –20, 0 and 40 °C under a nitrogen atmosphere with 30, 50 and 70 mol% of feed compositions in TBMA monomer. $^1$H and $^{13}$C NMR spectra were measured for 8 wt/vol% solution in CDCl$_3$ at 55 °C using a JEOL ECX400 spectrometer equipped with a 10 mm $^{13}$C-$^{15}$N{$^1$H} tunable probe. Bucket integration of the spectral regions 15.5 – 22.5 ppm (the $\alpha$-methyl carbons), 44.0 – 47.5 ppm (the backbone quaternary carbons) and 175.0 – 179.0 ppm

![Figure 1. (a) PC1-PC2 and (b) PC1-PC3 score plots for $^{13}$C NMR signals of the carbonyl, backbone quaternary and $\alpha$-methyl carbons of 12 poly(MMA-co-TBMA)s polymerized at –40 (□), –20 (▲), 0 (▲) and 40 °C (■). T3, T5 and T7 series indicate the feed compositions of TBMA monomer are 30, 50 and 70 mol%.

Figure 1. a) PC1-PC2 and b) PC1-PC3 score plots for $^{13}$C NMR signals of the carbonyl, backbone quaternary and $\alpha$-methyl carbons of 12 poly(MMA-co-TBMA)s polymerized at –40 (□), –20 (▲), 0 (▲) and 40 °C (■). T3, T5 and T7 series indicate the feed compositions of TBMA monomer are 30, 50 and 70 mol%.
(the carbonyl carbons) was performed at an interval of 0.01 ppm with JEOL Alice2 ver.5 for metabolome ver.1.6 software. Principal component analysis (PCA) and partial least-square regressions (PLSR) were conducted using Pattern Recognition Systems Sirius ver.7.0 software.

PCA of $^{13}$C NMR spectra of 12 copolymer samples gave first, second and third principal components (PC1, PC2, PC3) with contribution factors of 90.3, 5.4 and 2.7 %, respectively. Figure 1 shows the PC1-PC2 and PC1-PC3 score plots of their samples. The PC1 and PC2 mainly corresponded to chemical composition and heterogeneity of comonomer sequence, as shown in our previous report. The PC3 scores increased with decreasing temperature of polymerization. This suggests that the PC3 score mainly reflected stereoregularity, because syndiotactic specificity increases with decreasing temperature in methacrylate polymerization.

PLSR models were constructed with the $^{13}$C NMR spectra of copolymers and the fractions of $rr$, $mr$, $mm$ triads. The fractions of configurational triads were determined by $^1$H NMR spectra of PMMAs converted from the copolymers through hydrolytic cleavage of the tert-butyl esters and subsequent methylation with diazomethane. These models consisted of 10 copolymers excepting two T5 series copolymers prepared at −20 and 0 °C as “unknown samples” (see the caption of Figure 1 for the notation of T5 series). Figure 2 shows the cross validation of the PLSR models. Excellent linear relationships were obtained between the observed and predicted $rr$, $mr$, $mm$ triads, with a correlation coefficient ($R^2$) of 0.997 – 0.999 and a relative standard deviation (RSD) of 0.2 – 0.9 %. The predicted $rr$, $mr$, $mm$ triads of two “unknown samples” gave an RSD of 1.6 – 12.9 % with the PLSR models.

Figure 2. Cross validation of PLSR models for predicting fractions of a) syndiotactic, b) heterotactic and c) isotactic triad in poly(MMA-co-TBMA)s (●) and relationship between observed and predicted them in two T5 series copolymer prepared at −20 and 0 °C as “unknown samples”.

Adsorption of Chitosan on Oppositely Charged Monolayer at the Air-Water Interface: Structural Characterization by X-Rays.

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The aim of this research was to investigate the adsorption of chitosan, a pseudo-natural polyelectrolyte, on an oppositely charged surface consisting of a surfactant monolayer (behenic acid) at the air-water interface. The structure of the adsorbed layers and the effect of the net charge of the polymeric chains on the arrangement of the surfactant molecules in the monolayer were determined by surface sensitive synchrotron X-Ray techniques: Reflectivity (XRR) and Grazing Incidence Diffraction (GID).[1,2] The purpose was to study a model system in order to explain the adsorption mechanism and the structure of the adsorbed polyelectrolyte on the oppositely charged surface of a particle. The interfacial complex layer stabilizes the particles and protects their integrity against different stresses (pH, ionic concentration, osmotic shocks…). These systems formed may be used in many applications such as the fabrication of composite nanoparticles suitable for delivery and/or storage of drugs. Objects like micelles and nano- or microvesicles or capsules decorated with natural and biocompatible polyelectrolytes adsorbed at the interface may have controlled and tunable net charge by controlling the physicochemical parameters like pH and concentration of the polymer subphase.[3,4,5]

The thickness and the in-plane structure of the adsorbed layers were characterized by XRR and GID using synchrotron radiation at the European Synchrotron Radiation Facility. Obtained results show that the polyelectrolyte adsorbed to the surfactant monolayer as a thin film, the adsorption mechanism was studied too.

References

Rheological and Molecular Characterization of regraded Nylon-6
obtained in Different Reactive Compounding

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In order to evaluate the possibility of recycling post-industrial and post-consumer polyamide materials, a specific research was devoted to the regradation process of Nylon-6 (PA6) by using selected additives in reactive compounding. The presence of free amine and/or carboxyl end group in polyamide allows a chemical bonding between macromolecules. Three different additives were used and compared with respect to a commercial polyamide Aquamid AQ27000 (Aquafil S.p.A , Arco-Italy). In particular two reactive compounds, designated CBC (N,N’-carbonyl-bis-caprolactam) and PCPA (a masterbatch of low viscosity polycarbonate and polyamide with acid terminations) that react with amine groups; and 1,3-phenylene-bis-oxazoline (PBO) that specifically reacts with carboxy terminal ends.

Reactive compounding was performed by using an industrial co-rotating twin-screw extruder (Aquafil Engineering Plastics, Arco-Italy) with screw diameter of 42 mm and a L/D ratio of about 40. Melt compounding of polyamide with various amount of additives ranging between 0.1 and 2 wt%, was performed applying a barrel temperature profile from 230 to 260°C, a screw speed of 300 rpm, and a throughput of 120 kg/h.

The properties of regraded polymers have been evaluated and compared by rheological viscosity, determination of solution viscosity number, and titration of both amine and carboxy end groups.

Dynamic rheological tests were performed by using a Dynisco Polymer LCR 52M capillary rheometer (D=0.76mm, L/D =33; 260 °C; shear rate 100-10000 s⁻¹; residence times of 3 and 13 minutes) after drying in vacuum at 120 °C for 12 h.

Viscosity number according to ISO 307, was measured at 25°C in sulfuric acid (96%) at concentration of 0.01 g/ml. Specific titration of end groups after dissolution of about 0.8 g of polymer in 20 ml of 2,2,2 trifluoroethanol (TFE) at 55 °C was performed by using a Mettler DL50 automatic titrator, and HCl 0.02 N solution or NaOH 0.02 N solution for titration of -NH₂ or -COOH groups respectively.

PA6 processed with CBC or PCPA evidenced a progressive increase of apparent viscosity at 260°C in all the range of shear rate, as shown in Figure 1 (after 3 mins of residence time). The apparent viscosity was found furtherly higher for residence time of 13 mins. Rheological results were confirmed from end-groups titration, that evidenced a progressive reduction of -NH₂ groups, whereas
an almost constant value of –COOH was found, confirming the selective reactivity of CBC and PCPA. On the other hand, a lower efficiency of PBO was registered from both rheological and molecular analysis.

Fig 1. Rheological results of PA6 after regradation with CBC (0.1-0.4%) and PCPA (0.5-2.0%).

The viscosity number of PA6 after reactive processing with CBC, PCPA and PBO is reported in Figure 2. It is evident not only the different behavior of CBC and PCPA with respect of PBO, but also the higher efficiency of CBC.

Moreover, number of viscosity and titration of terminal groups of various polymers were also evaluated after different residence times in rheometer (3 and 13 min). Figure 2B revealed that significant variations occurred between chips, as obtained after compounding, and the polymers after rheometry at 260°C.

A further reduction of residual amino groups and a parallel increase of viscosity number was evidenced for nylon-6 regraded with CBC or PCPA. Some post-condensation reactions in the rheometer were evidenced, especially after 13 mins of residence time. A simple model for molecular weight prevision after reactive processing in dependence on type and the amount of the regrading compound will be also presented.

Fig 2. Viscosity number of PA6 after regradation with CBC, PCPA and PBO.
Effect of Block Composition and Molecular Weight on the Structure of Donut-Shaped Micelle

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The block copolymer is self-assembled into a micelle in a selective solvent. Recently, Huang et al. reported the highly uniform donut-shaped micelle from polyisoprene-block-poly(2-vinylpyridine) (PI-b-P2VP) in mixture solvent system. In this study, we have investigated the factors in the structural behavior of donut-shaped micelle such as block composition and total molecular weight of PI-b-P2VP.

We synthesized two series of PI-b-P2VP samples by anionic polymerization. Each PI-b-P2VP in the one series has the same total molecular weight but different block composition. And the other series exhibits the same block composition but different total molecular weight. The size of prepared micelle was characterized by using dynamic light scattering in solution state, and their structures were visualized by atomic force microscopy.

Generally, morphological changes of micelle are induced by different block compositions of diblock copolymer. However, donut-shaped micelle was shown in wide range of PI block composition from 0.5 to 0.8. And the hydrodynamic size of donut-shaped micelle depends on the total molecular weight.

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Table 1. Structural characteristics of two series of PI-b-P2VP samples and the hydrodynamic radius ($R_h$) of donut-shaped micelles.

Reference

Structural Characterization of \textit{Fddd} phase in Diblock Copolymer

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Block copolymers exhibit various nano-scale morphologies. In diblock copolymers, lamellar (LAM), hexagonally packed cylinder (HEX), spheres arranged in body centered cubic lattice (BCC), double gyroid (DG) and hexagonally perforated lamellar (HPL) phases have been well established. Recently another network phase was experimentally found in bulk state.\textsuperscript{1-4} It has an orthorhombic unit cell and belongs to the \textit{Fddd} space group (O\textsuperscript{70}).

\textit{Fddd} network structure of a polystyrene-\textit{block}-polyisoprene (PS-\textit{b}-PI) diblock copolymer ($M_\text{n} = 31.5$ k, $f_{\text{PI}} = 0.645$) was observed for the first time by transmission electron microtomography and grazing incidence X-ray scattering. In a 650 nm thick film of the PS-\textit{b}-PI thin film on a silicon wafer, \textit{Fddd} phase was developed after annealing at 215°C for 24 h. The single network structure consists of the connected tripodal units of minor PS block domains. The \{111\}_\textit{Fddd} plane, the densest plane of minor PS phase, was found to orient parallel to the film plane. The transitional structure from the wetting layer at the free surface to the internal \{111\}_\textit{Fddd} plane \textit{via} perforated layer structure is also observed.

\textbf{References}

Advanced Triple Detection GPC for accurate and complete characterisation of Nitrocellulose

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The complete characterisation of nitrocellulose is of particular interest with manufacturers to determine the properties and key parameters underpinning the role of the material in the final product formulation. This poster studies batches of nitrocellulose originated from two different sources that had significant performance differences in the final product. The first nitrocellulose was derived from pure wood pulp and the second from a blended cotton and wood linters source. Advanced triple detection GPC determines the correct molecular weight as well as showing significant structural differences between the two batches. This data is compared to RI only GPC and clearly highlights the limitations of using the conventional calibration method.
Innovative membranes development for fuel cells application

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From several years, our research group takes care about the synthesis, chemical-physical characterisation and in particular application of new proton conductive membranes based on both new organic polymer and polymeric blends with PEEK and PES as alternative to Nafion membranes.

Based on the interesting results obtained with sulfonated PEEK-WC (poly(oxa-p-phenylene-3,3-phtalido-p-phenylene-oxa-p-phenilene-oxy-phenylene)), further systems were studied in order to obtain new kind of conductive membranes with high chemical and thermal stability as possible alternative to Nafion membranes. Polymer blends of Nafion 117 were used in different concentrations of PEEK and PES, both sulfonated and non-sulfonated, in order to reduce the cost of membranes and to limit the methanol crossover.

Sulfonated polyaryletherketones and sulfones where chosen because they show a good chemical resistance to oxidation. The idea was to use two components, one for hydration and conductivity and the other for mechanical stability and limited methanol crossover.

The fabrication of these blends was done by casting them under controlled temperature and in the presence of a suitable solvent. The polymer blends created were PEEK-WC/ Nafion117, SPEEK-WC/ PES-WC, SPEEK-WC/ Nafion117, SPES-WC/ Nafion117, SPES-F/ Nafion117.

The characterisations of several blends are in progress concerning PEEK-WC/ Nafion117 blends in different concentrations, it was observed an uniformity and homogeneity of the membranes from a macroscopic point of view. However, from microscopic point of view, the results obtained from the characterizations (DMA, FT-ATR, DSC) show that the compatibility of Nafion and PEEK-WC is low. Above a certain threshold value, these molecules tend to form groups with each other in an inhomogeneous way resulting a decrease in the system performance.
PEEKs possess good thermal stability, appropriate mechanical strength and high proton conductivity, which depend on their degree of sulfonation (DS); it is well known that PEEK with high DS are water soluble and this leads polymers can not be used as membranes in fuel cells.

The mechanical and water solubility weakness of non-cross-linked sulfonated polymers initiated a number of attempts to prepare more stable and mechanically stronger cross-linked PEMs. Sulfonated PEEK can be conveniently partially cross-linked through bridging links to the reactive sulfonic acid functions.

The concept of cross-linked blend has been developed by Kerres [1] according to a model that provides the blend of a polymer functionalized with basic-groups (-NH$_2$) and an other one functionalized with acid groups (-SO$_3$H). The sulfonic group interacts through an ionic bond, which is due to acid-base system, with the amino group.

It is also possible to obtain corresponding sulfonamides by warming the membranes by elimination of water, thus obtaining a covalent network.

In order to exploit the greater activity of polymers having high numbers of sulfonic acid groups, the partial cross-linking of the sulfonated polymer with low mols percent of amino derivatives (PEEK-WC-NH$_2$) previously synthesized by our lab [2] was carried out.

The purpose was to decrease the methanol crossover, improve the mechanical properties and proton conductivity. The ionic bond might lead to the following results:

1. the compatibilisation of the blended polymers, which reduces swelling, improves mechanical properties and the decrease of methanol crossover through membranes.
2. the mixing of acidic and basic molecules generally forms a proton conductive pathway, and thus the blend with amine polymers will lead to the protons transfer from protonated-amine groups to the sulfonated groups of the polymer blends.

References


Morphological and chemical aspects evaluation of different wood species by spectral and thermal methods

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Wood is an abundant, renewable, and biodegradable composite with many useful applications, such as paper pulp production, building and furniture, natural reinforcement in polymer composites, and it is an important source of energy. The characterization of wood samples is a complex procedure involving several steps wherein wood components are isolated or degraded to monomeric fragments. The aim of this study is to find the most convenient procedure to make an easy differentiation between various kinds of wood.

The wood samples used were: hornbeam (Carpinus betulus), oak (Quercus robur), beech (Fagus sylvatica), walnut (Juglans regia), sycamore (Acer pseudoplatanus), sweet cherry (Prunus avium), lime (Tilia cordata), poplar (Populus tremula), fir (Acer alba). The methods of investigation used were FT-IR spectroscopy and thermogravimetry. It was observed that different wood species exhibit different characteristics in the same experimental conditions of analysis. This can be observed from not only one mode of analysis.

By FT-IR spectroscopy, was observed that the spectrum of fir (softwood) is quite different from the other spectra (hardwoods). The variation of the integral absorptions of the FT-IR bands, assigned to characteristic bending or stretching vibrations of different groups from cellulose are higher in hardwoods than in softwood sample. Despite many similarities across all spectra, analysis of peak ratios, which reflect relative shifts in chemical wood composition, revealed site-specific features. The ratio values of lignin/carbohydrate IR bands for wood decreases with increasing the average specific gravity. A significantly large decrease in the intensity ratio of lignin/carbohydrate band intensity from softwood to hardwoods shows a decrease in lignin content with increases the specific gravity of wood. Also, the calculated values of lignin percentage from the FT-IR spectra are in very good correlation with the values from literature (obtained by gravimetric methods).

Thermal analysis is able to give information about degradation temperatures for the principal components of different wood samples. The shape of DTG curves depends on the wood species that
cause the enlargement of the peaks or the maxima of the decomposition step varies at larger or smaller temperatures ranges. The temperatures and global kinetic parameters are particular for each kind of wood.

This study showed that analytical methods used have the potential to be important sources of information for a quick evaluation of the chemical composition of wood samples.

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Thermal behaviors of carbosilane dendrimers studied by FT-IR spectroscopy and thermogravimetry

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Dendrimers are interesting macromolecules owing to their well defined, highly branched structures and physical properties, and they have drawn the attention of chemical, biological and materials scientists for more than two decades. The propensity of dendrimers to enclose guest molecules and their potential application in drug delivery and gene therapy has been studied since the early developments in dendrimer chemistry. Dendrimers specifically designed for the molecular recognition of substrates, including chiral ones, are generally synthesized by connecting wedges (dendrons) to receptors. Within the different dendrimer families known, the carbosilane dendrimers form a special class. The physical properties of the carbosilane dendrimers, such as their viscosity, core-accessibility, the size of the internal voids and the generation at which surface congestion occurs, can be tuned easily by choosing the appropriate building blocks for the dendrimer growth sequence. Furthermore, carbosilane dendrimers are robust, highly apolar macromolecules with low glass transition temperatures.

In this study, a carbosilane dendrimer is investigated by differential scanning calorimetry (DSC), FTIR and 2D IR correlation spectroscopy. The sequential order of changes in the molecular environment and conformations of the functional groups is evidenced.

The dendrimer displays a main mass loss in the region 228–503 °C ($\Delta w = 70$ wt%). The final step is the high temperature degradation of these stabilized structures to yield volatile products and a small quantity of carbonaceous char.

The IR spectra of carbosilane dendrimers at higher temperatures were studied. Spectral modifications which occurred on heating process of the studied dendrimer are evidenced in the 2700-3100 cm$^{-1}$, 1175-1500 cm$^{-1}$, and 400-1500 cm$^{-1}$ spectral regions. Resolution enhancement techniques such as second derivative, spectral difference and deconvolution were used to identify the positions of the individual bands. The changes which occurred in the spectra could be due to the conformational
and/or structural modifications or to phase transitions. The different sensitivity with temperature of the functional groups is evidenced by plotting the integral absorption versus temperature.

At temperature $180\, ^\circ C$ the studied carbosilane dendrimers are stable when contact with atmosphere is absent, in the air they oxidize and thus C-O and Si-O groups appear.

Additionally, a more detailed study was carried out using 2D correlation spectroscopy. This method is particularly useful for the analysis of the highly overlapped bands and the determination of the sequential order of the intensity changes caused by temperature as external perturbation. During the sample heating the increase of the absorption band at $1047\, cm^{-1}$ is due to the ester group $H-C(O)-O-R$. The bands at $1445$, $1409$, $1268$, $1000–1100$, and $795\, cm^{-1}$, characteristic for the IR spectra of polysiloxanes $[-O-Si(Me)2-O-Si(Me)2-]x$ emerge. The addition contribution at $1050\, cm^{-1}$ is probably due to the $C\, O\, C$ ether fragments.

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