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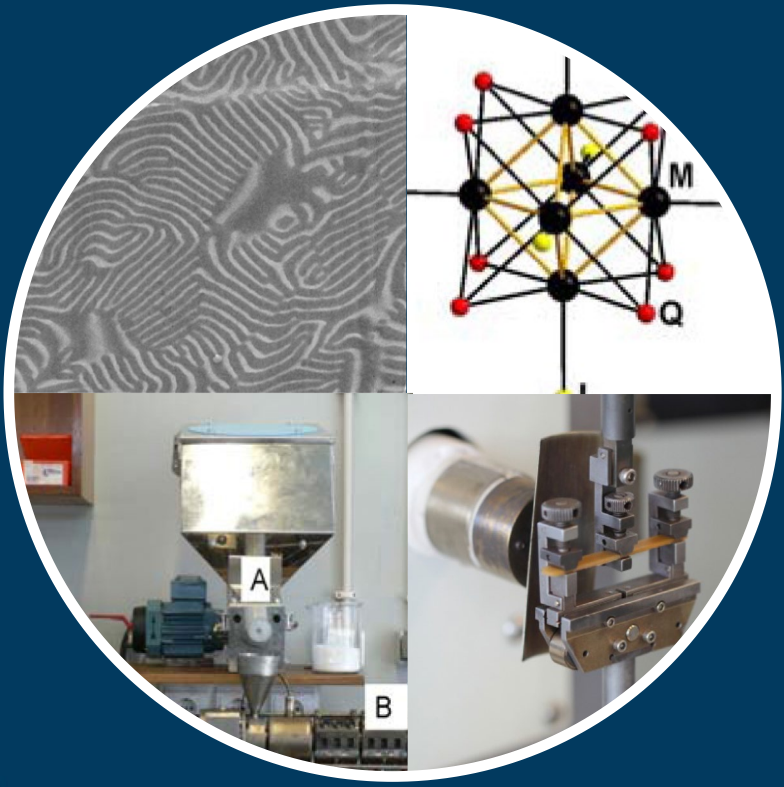
POLYMAR 2013

IST International Conference in Polymers with special Focus in Early Stage Researchers

José M. Lagarón, Luis Cabedo,
Amparo López, María J. Fabra (eds.)



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EDITORS' PREFACE

Dear Conference Attendee,

The organizing committee (IATA-CSIC, Universitat Jaume I, COST Actions FA0904, and MP1206, GEP and EPF) would like to welcome you to the international conference POLYMAR 2013. The POLYMAR 2013 conference is, to the best of our knowledge, the first conference in Polymers ever to be made on a boat across the Mediterranean Sea with special focus on Early Stage Researchers (ESR) with no nationality restriction.

The conference intends to provide a low cost all included forum for the polymer scientific community to meet up, show their latest work and activities and network with their peers. All attendees are expected to provide short talks, highlighting their main research results, interests and current activities of their groups.

Although the conference is intended primarily for young polymer scientists including young group leaders, permanent researchers starting their own groups, young academics being currently part of a group, post-docs and PhD and Master students, in fact, anyone working with polymers is welcome to join the conference. To provide an equal opportunity forum, there is no invited or keynote talks, everyone is at the same level and everyone has a say. A round table is programed one of the days to discuss the future of the field.

The conference is also intending, as any related conference, to gather a "snapshot" of what is currently exciting in the area and is also open to polymer scientists from industry. Getting value and perspective out of the significant knowledge coined over the years in the field is a major focus. The reason is that the macromolecular science field is currently very broad and many scientists not coming from the topic approach this to find complementarity to their research and technological activities. The field is thus consolidating as a cross-cutting and interdisciplinary area with people from areas such as the analytical field, medical, pharmaceutical, biotechnology, nanotechnology and food science and technology becoming more and more interested, especially in the design of applications. In the current depressing international environment for research activities, where national and industry funding is getting more and more scarce, it is a moment for the ESR community to get their acts together and in partnership find ways to take research into valuable action, either by grouping within international teams to tackle European or international Grand Challenge projects or by creating spin-offs to produce the next generation of technology based industries.

The present book is the compilation of the abstracts submitted by the conference delegates as delivered.

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POLYMERIZATION, POLYMER SYNTHESIS AND MODIFICATION

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EFFECT OF POLYDISPERSITY ON MORPHOLOGY OF STYRENE/METHYL METHACRYLATE DIBLOCK COPOLYMERS PREPARED BY RAFT COPOLYMERIZATION

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At present block copolymers are widely used in development of new materials with unique properties. It is connected with possibility of formation both in melts and in solutions of these copolymers of periodic structures of different morphology with a period of nano-size range.

The aim of the present work is the study of the dependence of the type morphology of block copolymers on polydispersity of them macromolecules. To solve this problem the diblock copolymers of styrene and methyl methacrylate with a well defined structure were synthesized by the two-stage reverse addition-fragmentation chain transfer radical polymerization (RAFT). At the first stage of the reactions we have prepared the poly(methyl methacrylate) block. The reaction was carried out in the presence of the initiator - 2,2'-azobis(isobutyronitrile) (AIBN), and low-molecular RAFT-agent - 2-phenyl-2-propyl benzodithioate. On the second stage diblock copolymers were synthesized by RAFT-polymerization of styrene in the presence of AIBN and poly(methyl methacrylate) RAFT-agent. The polydispersity of diblock-copolymers was adjusted by change of RAFT-agent concentration. Molecular-mass characteristics of the obtained polymers determined by gel permeation chromatography. ^{1}H-NMR-spectroscopy was applied to estimate the composition of diblock-copolymers.

For experimental studies of the morphology of the films synthesized samples PMMA-block-PST-copolymers, used the methods of transmission (transmission) of electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

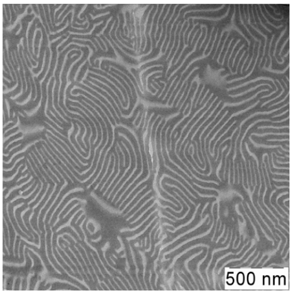

Figure 1. TEM-images of symmetric PMMA-block-PST copolymers with M_w/M_n=1.11

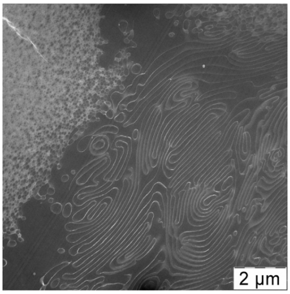

Figure 2. TEM-images of symmetric PMMA-block-PST copolymers with $M_w/M_n= 1.22$

TEM on solvent cast films of symmetric copolymers with narrow disperse distribution reveals lamellar morphologies (Figure 1). An increase of polydispersity up to 1.2-1.3 yields macrophase separation (Figure 2).

BIO-BASED COMPOSITE RESINS

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ABSTRACT

Most currently employed composite resins consist of polyester suspended in Styrene. The use of styrene is widely discouraged for environmental and toxic reasons. Various alternative systems have been investigated, some of which employ bio-based resources, reducing the carbon footprint and dependence on fossil fuels. However, at end of life these green resins still mostly end up in landfills or incinerators. To truly tackle this problem a sustainable end of life solution is needed. In this work, we present a polymeric system derived from mostly bio-based materials utilizing a different crosslinking chemistry altogether (eliminating styrene) making it capable of thermo reversible crosslinking. The material is proven to be recycled while preserving its mechanical properties proving a true cradle-to-cradle solution.

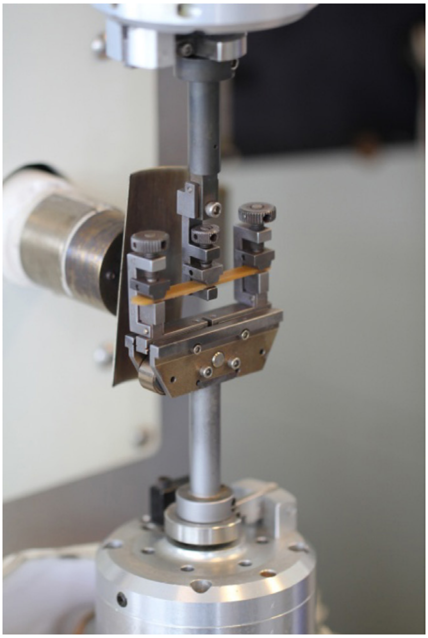

Figure 1. DMTA measurements show full thermal reversibility and reworkability

POLYSTYRENE-POLY(SODIUM METHACRYLATE) BLOCK COPOLYMERS BY ATRP: EFFECT OF BLOCK LENGHT AND MOLECULAR ARCHITECTURE ON RHEOLOGY OF THEIR WATER SOLUTIONS

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Amphiphilic block polyelectrolytes (ABP) such as Polystyrene-Poly(sodium methacrylate), are known to form stable micelles in water. The presence of these large aggregates, generally results in interesting interfacial and rheological properties, useful for many applications (e.g.: enhanced oil recovery, paints, drug delivery).[1] Despite the large number of publications concerning synthesis and self-assembly of various ABP, a systematic study of their rheology is still missing. The sparse literature is mostly limited to few diblock and telechelic Polystyrene-Poly(acrylic acid). To the best of our knowledge, the effect of block length or molecular architecture (e.g.: diblock vs triblock or star block) on the final rheological properties of ABP water solutions has not been investigated so far. Radical controlled polymerization methods (ATRP, NMP, RAFT) allow the synthesis of well-defined amphiphilic copolymers characterized by different molecular weight and structure.[2] These synthetic tools allow systematic investigations of the influence of molecular architecture on the chemical and physical properties of amphiphilic block copolymers. The knowledge of structure (rheological) properties relationship can be very useful in designing macromolecular structures for the desired application. For example water solutions of ABP can find use in enhanced oil recovery, provided that some requirements of viscosity, interfacial tension and salt sensitivity are met.

Here we describe the ATRP of some Polystyrene-Poly(sodium methacrylate) copolymers characterized by different molecular architecture (diblock, triblock and four arm star-block, see Figure) and by different length of hydrophobic and hydrophilic blocks. These polymers are studied from the point of view of their rheological properties in aqueous solution. All the studied systems form viscous solutions that present transition to a gel above a certain concentration. The dependence of sol-gel transition and gel strength from the molecular structure are discussed. A simple model has also been developed to qualitatively explain the observed data.

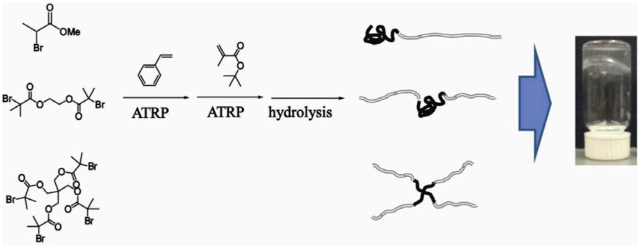

Figure 1. Representation of the synthesized polymers and picture of a typical gel formed in water, presenting a yield stress

Acknowledgments

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THE SYNTHESIS OF POLY (2-CHLORO-1,3-BUTADIENE) AND OTHER PRE-DEFINED POLYMERS USING RAFT CHEMISTRY

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Controlled polymerisation of 2-chloro-1,3-butadiene using reversible addition-fragmentation chain transfer (RAFT) chemistry has been demonstrated for the first time. 2-Chloro-1,3-butadiene (CB), more commonly known as chloroprene, has been used in the rubber industry for decades, namely as a cross-linked rubber. Industrially, poly(2-chloro-1,3-butadiene) (PCB) has applications as neoprene rubber throughout everyday life materials, for instance in adhesives and automobile components. Recent concerns over the rubber production process, especially concerning the additives used in cross-linking, has resulted in the demand for relatively low molecular weight, pre-defined poly(2-chloro-1,3-butadiene) to be furnished for cross-linking mechanisitic studies. To this end, four chain transfer agents (CTAs) in two different solvents have been studied in the design of an appropriate RAFT system.

The kinetics of these reactions are discussed and it is concluded that the ultimate successful system comprises 2-cyano-2-propylbenzodithioate (CPD) CTA in tetrahydrofuran (THF), which is able to control the synthesis of PCB homopolymers up to 50,000 g/mol molecular weight, with polydispersities (PDIs) <1.3.[1]

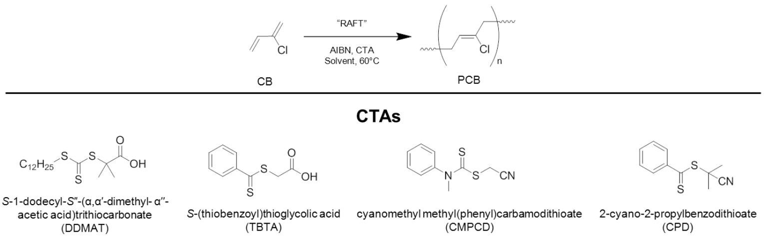

Figure 1. Polymerisation reaction scheme for 2-chloro-1,3-butadiene monomer (top) and the chain transfer agents used in this study (bottom

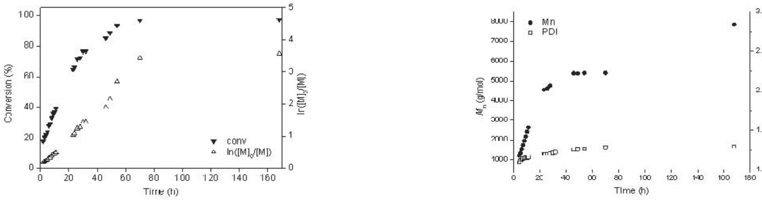

Figure 2. Kinetic plots for the polymerisation of 2-chloro-1,3-butadiene (CB) under the following conditions: $[AIBN]_0/[CPD]_0/[CB]_0 = 0.2/1/45$ at 60 °C in THF (50 wt%)

Acknowledgements

The authors wish to acknowledge Pera Technology, the European Commission and the EPSRC for supporting this work through a CASE studentship with Robinson Brothers Ltd and through funding as part of the Framework Programme 7 SafeRubber project (243756).

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2. Germack, D. S., and Wooley, K. L., *J. Polym. Sci., Part A: Polym. Chem.*, 45, 4100-4108, 2007.

POLY (β-L-MALIC AICD) ESTERIFICATION FOR NANOPARTICLE FORMATION AND DRUG ENCAPSULATION

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INTRODUCTION

Nowadays, biodegradation and bioabsorption of any high molecular weight material must be considered as a prerequisite for applications in medicine and pharmacology.1 In this regard, poly (β,L-malic acid) (PMLA) and its derivatives constitute a family of promising candidates. PMLA is a water-soluble, biodegradable, bioabsorbable and non-immunogenic polyester and its degradation produces easily metabolized L-malic acid.2 In this work we present nanoparticles of new derivatives of PMLA, which are attempted to be non cytotoxic, obtained by total or partial esterification of the carboxylic side group with ethanol or butanol, for the formulation of biodegradable nanoparticles which could be loaded with antigliomal drugs like Temozolomide (TMZ) or Doxurubicin (DOX).

RESULTS AND DISCUSSION

Ethyl and butyl PMLA esters with esterification degrees of ~50% and 100% were obtained. Reaction yields were around 50-70% with highest values afforded by reactions with ethanol. Hydrolytic degradation assays were carried at physiological pH (7.4, 37 °C) and at pH 5.0. Molecular weight of homopolymers decreased almost steadily with time, with a highest rate for ethyl derivative and for acidic medium. Degradation mechanism was studied by 1H NMR, showing first the hydrolysis of lateral chains and later the hydrolysis of the ester group from the main chain.

Spherical nanoparticles could be obtained with all polymers, with an average diameters between 140-340 nm (Fig. 1), however, in the case of PAALM-4 they did not showed a solid physical constitution, probably by its low T*g*. Drug release under physiological conditions showed a maximum TMZ release around 2 and 4 hours of incubation, with a release of 60% of the content in the case of *co*PAALM-H50Et50. PAALM-2 nanoparticles are the only ones that keep releasing TMZ after 48 h (Fig. 2), suggesting a major retention of TMZ and better hydrolysis protection to the drug, probably due to its hydrophobic character. In the case of DOX it presented a continuous release during the first 2-4 days to later stabilize but maintaining a small increment during the incubation time. Cytotoxicities of unloaded nanoparticles were practically negligible. In general all loaded NP needs more concentration to exert the same effect than the free drugs, nevertheless, *co*PAALM-H50Et50/Drug showed the closest behavior to free drugs. The most remarkable case is MDA-MB468 cell line treated with TMZ and TMZ-NPs, in which free TMZ shows ineffectiveness at all concentrations, while TMZ loaded nanoparticles reaches EC50 between 100-200 μM TMZ concentrations (Fig. 3).

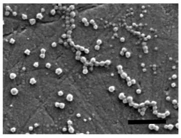

Figure 1. Copolymers nanoparticles:
a) *co*PAALM-H50Et50
y b) *co*PAALM-H50Bu50

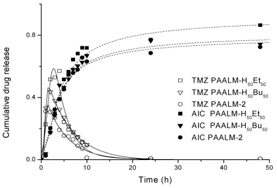

Figure 2. TMZ and AIC (degradation product) release

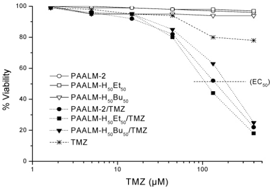

Figure 3. Cytotoxicity test on MDA MB468 cell line

CONCLUSION

PMLA was successfully esterified with ethanol and 1-butanol. Their hydrolytic degradation followed a typical mechanism initiated by lateral chain hydrolysis and followed by main chain break down. Nanoparticles (140-340 nm) could be formed by two different methods, and TMZ and DOX encapsulation was readily performed. Cyitotoxicity tests

revealed activity of the encapsulated drugs as well as improvement for TMZ response of the cell line MDA MB468.

Acknowledgements

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Authors are indebted to AGAUR (2012FI_B1 220) for grants awarded to A. Lanz.

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THE QUEST FOR A SAFER ACCELERATOR FOR CURING POLY (2-CHLORO-1,3-BUTADIENE)

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ABSTRACT

Poly(2-chloro-1,3-butadiene), more commonly known as polychloroprene, is also known by the trade name Neoprene. One distinguishing feature of polychloroprene is that it cross-links in a manner different to most other elastomers. Whereas most elastomers (such as natural rubber) use sulfur or a sulfur donor to cross-link the polymer, polychloroprene requires ETU (ethylene thiourea – Figure 1). ETU, however, is classified as a reprotoxic material and so will need to be replaced. To aid in finding a replacement for this hazardous material, the mechanism by which ETU cross-links polychloroprene alone, and in combination with zinc oxide (ZnO), needs to be fully elucidated.

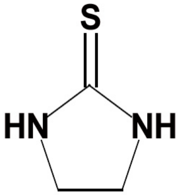

Figure 1. Structure of ethylene thourea (ETU)

The work herein gives a brief introduction to the rubber technology used in this project. Subsequently, using both spectroscopic and industrial rubber characterisation techniques, a new potential mechanism is outlined, which shows how ETU and ZnO cross-link polychloroprene.

From this new mechanism, and tests carried out with standard rubber accelerators, the building blocks of a new safer accelerator are deduced. Tests carried out with several different potential new accelerators are examined and those with the best results are compared to an ETU containing formulation. Finally, a new accelerator which displays similar properties to ETU is revealed for the first time.

Acknowledgements

The authors wish to acknowledge Pera Technology, the European Commission and the EPSRC for supporting this work through a CASE studentship with Robinson Brothers Ltd and through funding as part of the Framework Programme 7 SafeRubber project (243756).

TWO APPROACHES FOR INCORPORATING PHOTOLUMINESCENT OCTAHEDRAL MOLYBDENUM OR RHENIUM CLUSTER COMPEXES INTO ORGANIC POLYMERS

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INTRODUCTION

Octahedral molybdenum and rhenium cluster complexes of general formular $\{M_6Q_8\}Y_6$ (Fig.1) show bright photoluminescence in the red and near-infrared regions with high quantum yields and photoluminescence life times of 1-100 µs. Additionally, the cluster complexes are extremely robust, generate singlet oxygen efficiently, readily survive heating and photolysis. They also have the capability for undergoing reversible oxidation with retention of the original structure. The properties of the cluster complexes can be tuned readily simply by substitution of the outer ligands. Recent synthetic developments also mean that the cluster complexes can be afforded as soluble precursors for solution-based synthesis. Such a combination of physical and chemical properties make molybdenum and rhenium cluster complexes highly atractive for numerous of applications in biological sciences (e.g. bioimaging, biolabeling etc.) and as materials for light-emitting/harvesting devices (organic solar cells, OLEDs etc.). However, naked clusters are not ideally suited for any of these applications, as they must be supported by a media that tailors them to a certain application. Incorporating inorganic Mo/Re cluster complexes into organic polymer matrices offers great opportunities in terms of integrating the excellent photophysical properties of metal clusters with the bespoke properties of various organic polymer matrices and thus create designer materials tailored to specific applications.

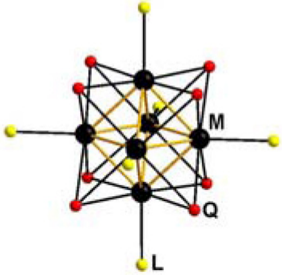

Figure 1. Idealised structure of octahedral [M6Q8L6] clusters, where M is Re/Mo, Q are halogens or chalcogens and L are terminal inorganic (OH, H2O, CN, Hal etc.), or organic (N, P, O dative atoms) ligands

RESULTS AND DISCUSSION

Recently we have developed two successful approaches for incorporating molybdenum and rhenium cluster complexes into conventional polymer matrices.

Approach 1: Initially, bespoke organic polymers are synthesised. These polymers are chemically functionalised so that they bear ligands for Mo/Re atoms metal cluster complexes. In a post polymerisation step the polymeric ligands are incubated with the metal cluster complexes resulting in irreversible incorporation of the clusters into the polymer matrix. To exemplify this approach, $(Bu_4N)_2[Mo_6I_8(NO_3)_2]$ cluster complex, bearing labile nitro-ligands, was synthesised. Styrene-based polymer microspheres functionalised with thiol groups (excellent binding agents for molybdenum atoms) were also constructed. The thiol-functionalised polymer microspheres were then incubated with a chloroform solution that contained the molybdenum cluster. The polymer microspheres bound to the clusters irreversibly via substitution of the labile NO_3 ligands on the cluster by sulphur atoms of the thiol groups within the microspheres. The $\{Mo_6I_8@PS\}$ microspheres are photoluminescent (λ=680 nm, Φ =0.04, τ=45, 16 and 2 μs), have a very narrow distribution of sizes (average size is 0.7 μm) and can be resuspended into both apolar and polar solvents without any leaching of the cluster moiety (Fig. 2). This new material is currently being evaluated for its utility in biomaging applications.

Approach 2: The second strategy centres on developing bespoke metal cluster complexes bearing polymerisable ligands for direct incorporation into polymers via co-polymerisation reactions. Recently we developed red-emitting cluster complexes *trans*-$Re_6Q_8(TBP)_4(4\text{-}VB)_2$ (Q=S, Se; TBP=*tert*-butylpyridine, 4-VB=4-vinylbenzoate) by the reaction of *trans*-$Re_6Q_8(TBP)_4(OH)_2$ with 4-vinylbenzoic acid. The complex exhibits bright red photoluminescence (λ_{em}=614nm, Q=S; λ_{em}=635nm, Q=Se,) and readily copolymerises with styrene and methyl methacrylate giving soluble, red-emitting polymers (M_n=19-22 kD for PS-based materials and M_n=23-26 kD for PMMA-based materials).

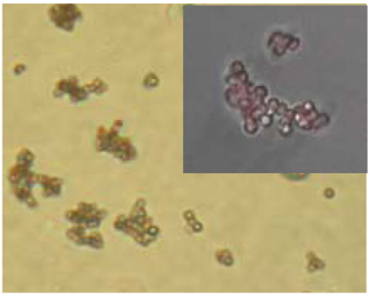

Figure 2. Optical and confocal (*insert*) microscopy images of {Mo6I8}@PS microspheres suspended in water

Acknowledgements

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THIOL REACTIVE POLYMERIC THIN FILMS FOR BIOMOLECULAR IMMOBILIZATION

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Conjugation of biomolecules onto surfaces using efficient methodologies are crucial to many applications such as fabrication of protein, nucleic acid or carbohydrate microarrays. Design of such platforms involve coating the surface with a reactive functional group that can undergo conjugation with a reactive group on the biomolecule. In this regard, the thiol maleimide conjugation reaction has been utilized for biomolecular immobilization since maleimide gives effective conjugation with thiols under mild condition. Over the past several years, we have focussed on development of polymeric constructs that contain thiol reactive maleimide units as side chains.[1,2]

In this study, we report design and synthesis of maleimide containing polymeric thin films and demonstrate their functionalization with thiol-containing molecules and ligands for bio-immobilization. For this purpose, PEG-based co-polymers containing reactive functional groups were synthesized and then coated on silicon oxide or glass surfaces. The maleimide group was masked using a furan group via the Diels-Alder reaction to protect it during the polymerization step.[3,4] These surfaces are rendered thiol-reactive upon heating by unmasking the maleimide group by removal of furan moiety via the retro Diels-Alder cycloreversion reaction. We demonstrate that patterns of bio-molecule can be easily fabricated on these reactive surfaces via micro-contact printing. Furthermore, the degree of immobilization onto such polymeric surfaces can be tailored by adjusting the amount of reactive functional group in the parent polymers.

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SURFACE DECORATION OF HYBRID POLYMERIC PARTICLES

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INTRODUCTION

The last few years, magnetic nanoparticles have attracted significant attention as advanced materials in applications such as magnetic resonance imaging (MRI), hyperthermia therapies, drug delivery, data storage or catalysis. Several articles deal with the incorporation of magnetic nanoparticles into crosslinked polymeric particles, thus leading to the formation of core–shell structured composite microspheres. Besides, the control of the surface functionalization of these microspheres commands the interactions between the material and the medium and also defines the ultimate applications. The surface functionality can be designed in the synthetic procedure of the microspheres, for instance using functional monomers. However, in this case the synthetic procedure should be optimized for each functional monomer, which is tedious, time-consuming and expensive. In contrast, the control of the chemical functionality by post-modification of the particles permits the preparation of a wide range of functional particles from a particular precursor.

RESULTS AND DISCUSSION

The decoration of polymeric magnetic particles has been done by two approaches (Figure 1): the first one consists on the decoration with glucose through the p-fluorine-thiol click reaction of divinylbenzene-*co*-pentafluorostyrene particles synthesized by precipitation polymerization with β-D-thioglucopyranose and in presence of magnetite nanoparticles (Fe_3O_4). And the second approach involves the decoration with gold nanoparticles through catechol chemistry between the divinylbenzene-*co*-dopamine methacrylamide particles with an aqueous solution of $HAuCl_4$. Primarily, the magnetic nanoparticles have been prepared by a thermal decomposition process followed by their modification with dopamine methacrylamide to incorporate vinyl groups at the nanoparticle surface.[1, 2] In the case of glycoparticles, their ability to specifically interact with Concanavalin A lectin has been studied by fluorescence spectroscopy. The second methodology allows the catechol groups at the particle surface to stabilize the nucleation and growth of gold nanoparticles and therefore, their use as catalysts. Their activity has been analyzed by studying the reduction reaction of nitrophenol to aminophenol by UV-Vis spectroscopy.[3]

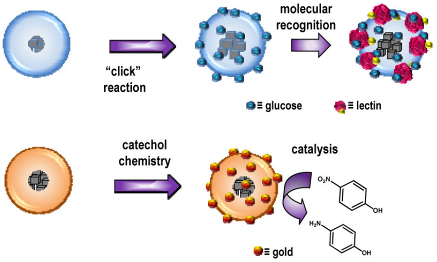

Figure 1. Schematic illustration of decorated particles

CONCLUSIONS

The resultant functional particles present potential interest in recognition processes and catalysis with the advantage of an easy removal from the media because of their magnetic properties.

Acknowledgments

MINECO is acknowledged for the financial support (MAT2010-17016). MAP and AMB GM thank MINECO for the FPI grant and Juan de la Cierva contract and GM thanks CSIC for her JAEdoc contract.

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CONTENTS

FACILE SYNTHESIS OF POLYMER-PEPTIDE CONJUGATES *VIA* DIRECT AMINO ACID COUPLING CHEMISTRY

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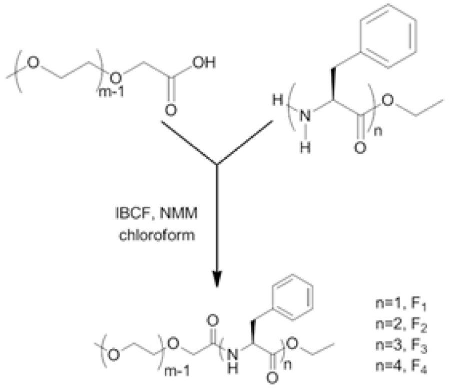
Polymer–peptide conjugates (also known as biohybrids) are attracting considerable attention as injectable materials owing to the self-assembling behavior of the peptide and the ability to control the material properties using the polymer component. To this end, a simple method for preparing poly(ethylene oxide)-oligophenylalanine polymer–peptide conjugates (mPEOm-Fn-OEt) using isobutylchloroformate as the activating reagent has been identified and developed. The synthetic approach reported employs an industrially viable route to produce conjugates with high yield and purity. Moreover, the approach allows judicious selection of the precursor building blocks to produce libraries of polymer–peptide conjugates with complete control over the molecular composition. Control over the molecular make-up of the conjugates allows fine control of the physicochemical properties, which will be exploited in future studies into the prominent self-assembling behavior of such materials.

We extend the applicability of solution-based amino acid coupling chemistry to produce simple, low molar mass polymer–peptide conjugates (Scheme 1). Solution phase synthesis negates the need for specialized equipment and is extremely simple for the formation of small oligopeptide-based materials. mPEO and oligophenylalanine have been selected to demonstrate this chemistry, where the individual component sizes have been systematically varied.

Utilizing IBCF with a carboxylic acid to join a peptide and polymer exemplifies a quick, clean strategy that extends the toolbox of available coupling chemistries, particularly useful for the rapid synthesis of simple polymer–peptide conjugates.



Scheme 1. Synthetic strategy for the preparation of mPEOm-Fn-OEt polymer-peptide conjugates using IBCF coupling chemistry.[1]

Acknowledgements

PDT thanks the Royal Society for partially funding this work through a Royal Society Research Grant.

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NANOPOROUS HIBRID MATERIALS AS METALLOCENE CATALYSTS SUPPORTS IN POLYETHYLENE POLYMERIZATION

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Polyethylene, polypropylene and copolymers has been industrially produced using metallocene catalysts on a small scale due to problems such as the polymer morphology control with soluble catalysts and the high quantities of co-catalyst to obtain high catalytic activities. The heterogeneous systems has been presented as a solution to the implementation of metallocene catalysts on a large scale.

The heterogeneous catalytic systems based in metallocenes have been and remain the subject of numerous investigations due to its low catalytic activity compared with homogeneous systems. This low catalytic activity is caused for the diffusion restrictions imposed by the support. Finding systems that allow heterogeneous catalytic mitigate this effect has been one of the major research challenges.

The importance of the support in the catalyst system is its influence on the catalytic activity of the catalyst and the morphology and properties of the polymer produced. Its chemical composition, surface area and morphology are important parameters in their choice.

The supports most commonly used in heterogeneous catalytic are silica, zeolites, alumina, clays, synthetic polymers and mesoporous materials. The amorphous silica has been used extensively due its high superficial area and high porosity. Supports such as alumina and magnesium dichloride have been used due its high pore distribution and amorphous structure. Other supports, among them zeolites and mesoporous materials, such as MCM (mobil composition of matter) and SBA (Santa Barbara Amorphous), have been less investigated.

Mesoporous materials and zeolites have structural and superficial properties that positively affect the catalytic activity of metallocene. Research results evidenced that textural properties of the ordered microporous and mesoporous supports influence the structure of the supported metallocenes and, therefore their catalytic activity. In this sense, supports with narrower pore diameters presented lower catalytic activities suggesting the higher probability of inactive bimolecular species formation due to the proximity among the catalytic precursors supported within micropores. Smaller pores also contribute to the formation of surface obstacles, which may hinder reactant diffusion. These considerations make ordered porous aluminosilicates more attractive for their application as metallocene supports, since they have larger pores (2–10 nm), which could enable metallocene and MAO molecules to be anchored not only on the surface but also inside the porous structure leading to polyethylene chains grow.

Currently hybrid suports (combination for zeolites/mesoporous silica or two-pore-size mesoporous silica) are being investigated in order to exploit their combine properties in the catalytic activity of metallocenes. In general, results show high activities in ethylene polymerization, providing an interesting investigation trend in this field. Due to the interest in different application domains, porous materials with divergent properties, specifically adjusted to catalytic uses, a lot of research is put into the development and controlled modification of these materials.

In recent years, a number of strategies has been reported to introduce zeolitic features into mesoporous alumino- silicates: dual templating, partial recrystallization of the pore walls, coating of the amorphous walls of the mesoporous materials with pseudo-zeolitic units, or the assembly of preformed nanoclustered zeolite seeds. The design of hibrid pore systems using sol-gel methods combined with surfactants as templates is a suitable route to obtain this kind of materials, as well as mesoporous materials with bimodal pore distribution.

Hybrid micro-mesostructured materials as supports of metallocene polymerization catalysts have exhibited the best catalytic activity in recents investigations. Combined micro and mesoporous materials were claimed to have advantages compared to the exclusively microporous or mesoporous materials; they provide improved diffusion rates for transport in catalytic processes and better hydrothermal stability. In general, catalysts with larger pores have presented higher activity in ethylene polymerization despite the presence also of smaller pores like in catalysts prepared with combined pore size distribution supports.

CONTENTS

SULFONATED POLY(HEXAMETHYLENE TEREPHTHALATE) COPOLYESTERS

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INTRODUCTION

Ionomers are compounds of great technological interest due to the fact that the ionic groups can interact with each other disturbing the supramolecular structure and modifying their physical and mechanical properties.[1,2] In order to improve the thermal and mechanical properties of poly(hexamethylene terephthalate), we have modified this polyester by copolymerization using 5-sodium sulfoisophthalate (SI) as comonomer in different proportions.

RESULTS AND DISCUSSION

Poly(hexamethylene terephthalate-*co*-hexamethylene 5-sodium sulfoisophthalate) (PHT$_x$SI$_y$) copolyesters containing from 5 to 50 mol % of sulfonated units, as well as the two parent homopolymers, were prepared by melt polycondensation according to the scheme depicted in Figure 1.[3] All they were obtained in high yields and with molecular weights decreasing with the increased content in SI units.

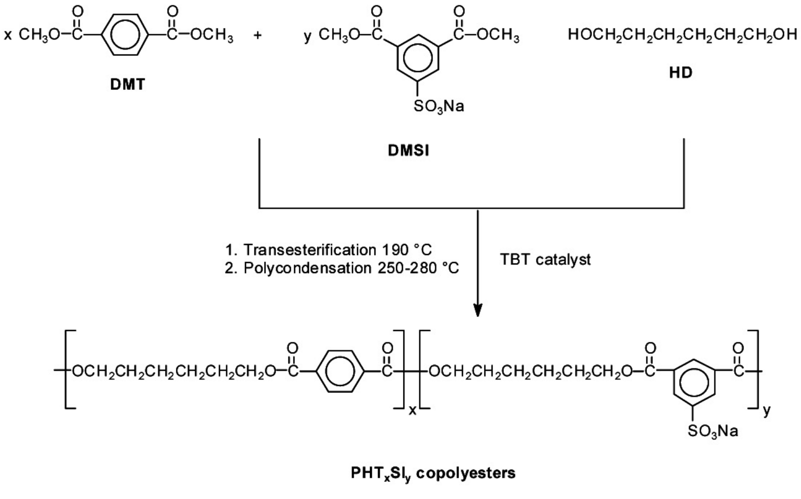

Figure 1. Outline of the synthesis route followed for the preparation of PHT$_x$SI$_y$ copolyesters

The effects provoked by the incorporation of SI units on the thermal properties were investigated by DSC and TGA. Copolyesters with SI contents equal or above 20 mol % were unable to crystallize from the melt so they remain amorphous after cooling to room temperature. For semicrystalline copolyesters, the melting temperature and enthalpy decreased gradually with the content in SI units. On the other hand, an increase of the glass transition temperature was observed with values ranging between those observed for the PHT and PHSI homopolyesters. The TGA data showed that PHT degraded in a single step, whereas the copolyesters and PHSI showed two or three steps depending on their composition.

The mechanical parameters, such as the Young's modulus, the maximum tensile stress and the elongation at break were affected by the incorporation of the ionic groups. It could be observed that the modulus increased gradually with the content in sulfonated units. The ionic interactions between the SI units, which restrict the mobility of the chains, seem to be the main factor responsible for this behavior.

Acknowledgments

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CONTENTS

CHARACTERIZATION, STRUCTURE-PROPERTIES AND SIMULATION

CONTENTS

COMPARISON OF DIFFERENT LIGHT SCATTERING TECHNIQUES FOR DETERMING POLYMER MOLECULAR WEIGHT AND SIZE

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Gel-Permeation chromatography is a well-established technique for measuring the Molecular Weight and Molecular Weight distribution of polymers. Historically, the retention volume of a series of known molecular weight standards were recorded and a calibration line constructed from which these properties could be obtained. However, this so-called "conventional calibration" technique is limited by the structural differences between the standards and the samples being measured. This means that any information produced by this method is only relative to the standard which was used. Importantly, the greater the difference in the structure between standard and sample the greater the difference in relative molecular weight from the real molecular weight of a sample.

With novel polymers becoming more and more common and the lack of availability of molecular weight standards for anything but simple polymers, static light scattering offers an alternative route to determine molecular weight independent of sample retention volume. Static light scattering detectors measure the intensity of light scattered by the polymer as it elutes from the column. The intensity of this scattered light is proportional to the molecular weight and concentration of a sample, with higher molecular weight molecules scattering more light.

Since light scattering detectors were introduced, they have seen several different development iterations. Modern systems are now either based on the RALS/LALS single angle approach or the MALS (multi-angle) approach. The former is often combined with a viscometer detector and hence also leads to choice between Rg and IV for determining structural differences in polymers. The introduction of a viscometer also allows detailed structural information of a polymer to be generated in a single GPC measurement which can be compared with other samples in Mark-Houwink plots.

This presentation will compare and contrast different methods for making light scattering measurements of molecular weight and also compare the resulting size data with size from intrinsic viscosity. The results from each will be examined to determine whether the full range of measurements can further increase the potential of light scattering and multi-detector GPC to gain further insights into the mass, size and structure of novel polymers.

RELATING STRUCTURE TO RELEASE RATE FOR Γ-IRRADIATED HGH CONTAINING PLGA MICROPARTICLES: ATR-FTIR IMAGING STUDY

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INTRODUCTION

A novel sustained release formulation of human growth hormone (hGH) prepared by supercritical fluid processing of PLGA/PLA/Poloxamer (the CriticalMix™ process) was produced in the form of microparticles (~100 µm), with demonstrated controlled release *in vitro* and *in vivo* via a hydrolytic degradation mechanism, offering a solution to the problem of rapid clearance of protein based drugs from body after injection [1]. In this work we demonstrate mid-infrared spectroscopic imaging coupled with multivariate image analysis to facilitate the understanding of the effect of γ dose on the controlled release behaviour of hGH from single microparticles of this multicomponent biodegradable polymer system.

RESULTS AND DISCUSSION

Microparticles (consisting of 10% (hGH), 81% PLGA:PLA(90:10) and 9% Poloxamer407) were subjected to doses of 0, 25 kGy (industrial sterilisation standard) and 100 kGy γ-irradiation. The release of hGH into D_2O at 37 °C from individual microparticles was monitored for 2 weeks using mid-IR imaging in ATR mode. In order to extract quantitative information from the temporal IR images (Figure 1.a) of this rather complex system, with decreasing S/N over days we developed a hard modelling routine that is able to deconvolute the contributions of the components.

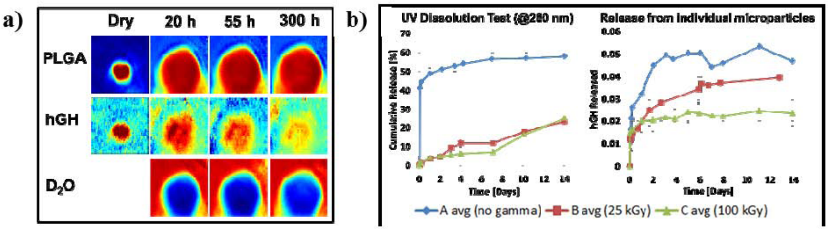

Figure 1. a)Temporal ATR-FTIR images where red colour is proportional to absorbance, showing the PLGA, hGH and water distribution from top to bottom at increasing time points from left to right, respectively. b) hGH release profiles obtained by conventional dissolution test on the left and release profiles obtained from mid-IR images of single microparticles undergoing dissolution in water on the right

CONTENTS

As shown in Figure 1.a, spatiotemporal FTIR images facilitate determination polymer morphology (swelling of PLGA/PLA), redisrtibution of hGH due to being released and water distribution surrounding the particle for the first time providing an insight to the effect of γ-irradiation on microparticles. Monitoring the decrease in deconvoluted protein amide I band over time, from 5x5 pixel averaged areas of the IR images, the release profiles of indivual microparticles are plotted in Figure.1b (right handside graph) which are in agreement with standard dissolution profiles showing γ-irradiated particles releasing hGH slower than that of non-irradiated (Figure1.b, left handside graph).

CONCLUSION

γ-irradiation was shown to delay the release of hGH from the microparticles a finding which is in agreement with those of Dorati *et al.* [2] who used ovalbumin as a model protein and in agreement with standard dissolution measurements we have performed on the same samples. This retardation of protein release is thought to be the result of two factors; (i) an increase in the number of oxygenated end-groups increasing the strength of interactions between the protein molecules and the PLGA/PLA polymer chains and (ii) a clear indication by SEM micrographs of a modification of the surface topography (smoother surface, more particle aggregation and lower porosity) as a function of γ-irradiation dose.

Acknowledgements

Authors would like to thank EPSRC of UK (grant no: EP/I501665/1) for supporting this work.

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MOLECULAR AND MECHANICAL ANALYSIS OF THE PHOTODEGRADATION OF A LOW-BANDGAP POLYMER

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The increasing world energetic demand has created a dependence to non-renewable sources that is not sustainable, therefore focusing the attention in the development of renewable energies. Due to the high theoretical potential and availability of solar energy, several efforts have already been made to exploit it. The photovoltaic technology mostly developed nowadays is based on silicon panels; however, their high production and installation cost creates the need for new solar technologies. A promising approach to this problem is organic photovoltaics (OPVs), characterised by low production costs and several interesting properties like flexibility, light weight, transparency or coloration. During the last decade, much effort has been made to improve the efficiencies of organic photovoltaics. With this aim, new conjugated polymers with bandgaps below 1.6 eV (low band gap polymers) have been synthesised, reaching efficiencies that nowadays overpass 10% [1]. However, the lifetime of organic photovoltaic devices is still insufficient to allow them to enter the market. In fact, one of the major problems is the stability of these polymers against external stress factors, such as UV-visible light, oxygen, or heat [2].

In this work, we report the behaviour of the low-bandgap polymer Si-PCPDTBT (poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-*alt*-4,7-(2,1,3-benzothiadiazole)) under different accelerated ageing conditions. To this end, thin films of neat polymer are deposited on transparent substrates, aged and monitored using a range of analytical techniques. Irradiation of the samples in ambient air is found to have the greatest impact on the chromophoric system, leading to complete bleaching of the polymer within several days, as followed by UV-Vis spectroscopy. The spectral distribution of the irradiation device is found to significantly influence the photo-oxidation kinetics. On the other side, the absolute degradation rate does not depend on the layer thickness. Infrared spectroscopy, in combination with chemical derivatisation treatments, is used to monitor the evolution of the different moieties in the polymer, as well as the development of new bands related to oxidation products. SPME-GC-MS analysis is employed to identify several volatile products and a degradation mechanism consistent with computational studies is proposed. Atomic Force Microscopy analysis verifies an increment of the surface roughness and stiffness during ageing. Irradiation in absence of oxygen is to found highly reduce the degradation rate.

Acknowledgements

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PERKINELMER INSTRUMENTAL SOLUTIONS FOR MATERIALS CHARACTERIZATION

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PerkinElmer offer a broad range of instrumental solutions for materials characterization, from the thermal analysis techniques to spectroscopy instruments.

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Hyphenated techniques couple two instruments together to gain insights into chemical structure previously unseen by either technique on its own.

Figure 1. FT-IR Microscopy
Spotlight 400

Figure 2. TG-IR-GCMS

CHARACTERISATION OF INTERVERTEBRAL DISCS USING FTIR MICROSCOPIC IMAGING

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Lower back pain affects millions of people worldwide, and has been linked to degenerative changes in the intervertebral disc (IVD) of the spine. In the 'NPmimetic' project, a multidisciplinary team has come together to develop a biomimetic nano-polymer based gel for minimally invasive disc regeneration treatment based on a novel electro-spinning technology. The biodegradable nano-fibres of the implant can also be designed to carry anti-inflammatory drugs, which can be released in situ promoting healing and preventing inflammation (http://npmimetic.com/). In this study we use FTIR microscopic imaging to obtain chemical maps of natural IVD material.

INTRODUCTION

An IVD consists primarily of a proteoglycan-water gel embedded in a randomly arranged collagen network. Fourier Transform Infrared Red (FTIR) microscopy in transflection-mode is used to generate chemical distribution maps from unstained paraffin embedded cross-sections of goat IVD samples. One microscopic image covers only a very small area (350 x 350 µm) of an IVD sample (~2.8 x 2.3 cm). Bigger areas are measured by sequential sample movement and image acquisition covering a user defined mosaic image area. FTIR mosaic imaging generally generates many thousands of data points. A major challenge is handling and analysing such large and chemically complex data sets in order to extract meaningful information. Using Iterative Multivariate Curve Resolution (MCR) techniques on the reduced data matrix from PCA analysis of 2nd derivative spectra it is possible to deconvolute highly overlapping IR peaks into single contributions of different molecular species.

RESULTS AND DISCUSSION

The chemical identity of the extracted component using an Iterative MCR algorithm is determined by comparing the extracted spectral profiles with the spectral profiles of reference materials for proteoglycan and collagen. Spectral features matching typical proteoglycan and collagen spectral characteristics are observed. The distribution of the extracted MCR factors for collagen and proteoglycan are shown in Figure 1 A. B. and can now be compared to consecutive cross sections which were stained using traditional histological methods. C and D.

show Masson trichrome staining for collagen and Alcian blue staining for proteoglycan. A good match can be seen between the extracted and stained distribution maps.

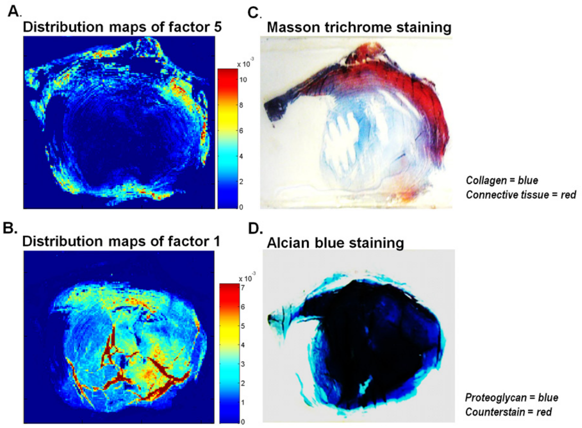

Figure 1. Distribution maps of Collagen and Proteoglycan

CONCLUSION

FTIR microscopic imaging in transflection-mode has been successfully used to generate molecular images of the collagen and proteoglycan distribution of natural IVD material without the use of contrast-enhancing agents. Furthermore, the use of 2nd derivative spectra together with the application of iterative MCR algorithms shows great potential to enhance the chemical specificity of FTIR imaging and opens up the possibility to distinguish between different proteins as well as their secondary structure, which are expressed only through minor peak shifts.

Acknowledgement

We thank the European Union (NPMIMETIC ref 246351) for 7th Framework Programme funding.

INFLUENCE OF PREHISTORY ON CRYSTAL NUCLEATION AND GROWTH

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Crystal nucleation and growth processes play a fundamental role in materials science determining widely the properties of broad classes of materials. By this reason, a variety of analyses is devoted to the description of crystallization processes in polymers ranging from classical theory of nucleation growth to field-theoretical approaches and computer modelling. However, in these approaches, so far no rigorous quantitative description of the influence of the prehistory-dependence of the glass or the polymer melt on crystal nucleation and growth is developed although a variety of experimental data exist indicating the deep connection between nucleation-growth rates and pre-treatment [1]. In the glass transition range as well as in the melt above the melting temperature, the structure of a polymer does not depend only on the actual values of the thermodynamic control parameters but also on the pre-history, i.e., on the evolution path the melt is brought into the respective state. By this reason, the crystallization kinetics has to depend on the prehistory of the systems as well. We present data on nucleation and crystallization kinetics of polymers depending on the actual state of the glassy polymer below T_g (PCL) [2] and depending on the entanglements in the melt above T_m (PE). In both experiments a non-equilibrium state is generated by fast (100,000 K/s) cooling or heating the sample to a temperature where the sample is allowed to relax towards equilibrium. The influence of the actual non-equilibrium state on crystal nucleation is studied by fast scanning calorimetry [3]. Different states in the glassy polymer are investigated on heating (cold crystallization). Differences in the entanglement density are observed on cooling (melt crystallization). For the latter experiments the starting material is a non-entangled high molecular mass polyethylene and the re-entanglement of the polymer melt with time was studied.

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ISOTACTIC POLY(PROPYLENE-*CO*-1-PENTENE-*CO*-1-HEXENE) TERPOLYMERS AND THEIR CRYSTALLINE POLYMORPHS

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Metallocene isotactic copolymers of propylene with high contents of 1-hexene (cPPHe) or 1-pentene (cPPPe) as comonomers exhibit a new polymorphic form [1-3]. Specimens slowly or isothermally crystallized develop the α and/or γ forms of isotactic polypropylene, iPP, for comonomer contents lower than about 10 mol %, whereas they crystallize in the new trigonal form at higher 1-hexene and 1-pentene concentrations. Scenario is somehow different in fast cooled samples. The monoclinic (and/or orthorhombic) crystals are not the only competitors of this trigonal phase but the mesomorphic form is also playing a primary role in this composition range [4]. Then, at the lowest comonomer contents, the monoclinic form is primarily developed (gathered with a reduced and variable amount of orthorhombic polymorph) while copolymers with molar compositions ranging around 5 to 10 are able to generate easily the mesomorphic structure.

What would it occur if both counits were involved, *i.e.*, if terpolymers were synthesized instead of cPPHe or cPPPe copolymers? Terpolymers based on propylene with 1-pentene and 1-hexene as comonomeric units are described in this work [5]. The trigonal polymorph is observed in rapidly cooled films with a global content in comonomers of about 14 mol %. A competition occurs between α/γ crystallites, mesomorphic entities and trigonal δ crystals in the composition interval below 14 mol % here also analyzed (see Figure 1 below).

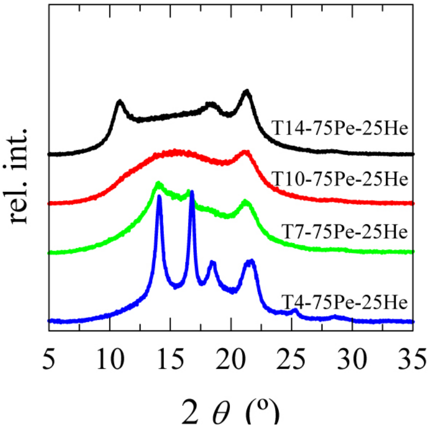

Figure 1. X-ray profiles, at room temperature, for the terpolymers (rapidly cooled from the melt) at different overall composition and at identical 1-pentene/1-hexene ratio (75:25). From bottom to top: T4-75Pe-25He, T7-75Pe-25He, T10-75Pe-25He and T14-75Pe-25He, respectively

Acknowledgements

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KINETICS OF THERMAL DECOMPOSITION OF POLY (3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) (PHBV): EFFECT OF PROCESSING AND CHAIN EXTENDERS

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Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biopolyester that is gaining much attention recently because of its origin from renewable resources and high temperature resistance and stiffness. Due to the fact that it is a biodegradable material, it could be a potential candidate to replace some commodities in the field of packaging industry. However, it presents some drawbacks (i.e. brittleness, low melt viscosity and or thermal degradation) that prevent its use in a broad range of potential industrial applications. Thermal degradation in PHBV is critical in multi-step industrial processing [1], like extrusion-thermoforming, widely used in the packaging industry.

To overcome the thermal stability issues, reactive extrusion technology has been used adding chain extenders. This type of stabilizers can be a good solution to balance complex PHBV formulations (with nanoclays, plastifiers, etc.) oriented to thermoforming [2]. It is reported that the main thermal degradation mechanism for PHBV is thermal hydrolysis by random chain scission [3]. However, it is essential to know the thermal degradation kinetics of PHBV with the addition of chain extenders, validate its viability as a high temperature thermal stabilizer and optimize the formulations. This work intends to investigate the degradation kinetics of a virgin (PHBV-p) and processed PHBV (PHBV-neat) with two different chain extenders (PHBV-TNPP and PHBV-JON) (Fig. 1 and Table 1). Different methodologies to assess the activation energy and order of reaction are presented: Coats and Redfern [4], Kissinger [5] and Kissinger-Carrasco [6], Horowitz and Metzwer [7] at a heating rate of 10ºC/min and the Maxfly-Wall-Ozawa [8, 9] approach with hating rates of 5, 10, 25 and 50 ºC/min.

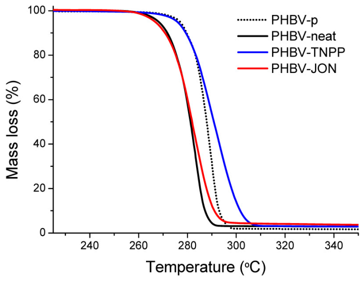

Figure 1. TGA curves

Table 1. Onset and 1st derivative peak temperatures form TGA data

Sample	T_{onset} (ºC)	T_p(ºC)
PHBV-p	277	291,6
PHBV-neat	268	284,9
PHBV-TNPP	276	294,5
PHBV-JON	266	285,6

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Acknowledgements

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CONTENTS

DIFFUSIONAL AND SURFACE PROPERTIES OF ELECTROSPUN POLY (ε-CAPROLACTONE) NANOFIBERS WITH TRYPSIN ENCAPSULATION

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Electrospun Nanofibers (ENf) find applications in several areas, such as biomedical, tissue engineering, pharmacology and also food engineering. One of the most important features is the ability of the ENf to serve as a filtration membrane as well as a catalytic surface. The pore size and the ability to encapsulate enzymes within the nanofibrous membrane will render them able to have a double function when in the presence of suitable molecules. To optimize the fabrication methods as well as the development of ENf in food engineering, some material properties and functions must be studied. This work focused in the diffusion properties of simple Poly ε-caprolactone nanofibers (PCL membrane), and Poly ε-caprolactone nanofibers with trypsin encapsulated, (E_PCL membrane), as well as ENfs' surface properties. Bovine serum albumin (66.5 kDa), lactoferrin (80 kDa), lysozyme (14.7 kDa), were the solutes chosen for effective diffusivity (*D*) evaluation. An acrylic diffusion cell with flow recirculation was used to determine *D* for the various solutes and systems. Subsequent analyses of the ENf were made by Contact Angle measurements (CA), Differential Scanning Calorimetry (DSC), Termogravimetric Analysis (TGA), Water Solubility and Swelling Degree (SD) and Mechanical properties assessment.

High hydrophobicity values of PCL were observed and the E_PCL membrane revealed stronger mechanical properties and an increase of mass due to water incorporation; SD (PCL)

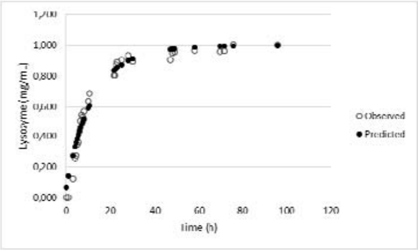

Figure 1. Model fitting for Lysozyme diffusion in E_PCL

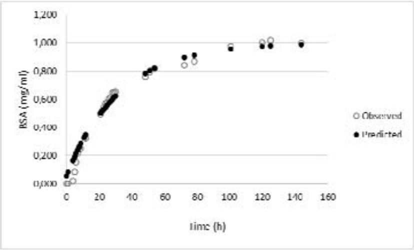

Figure 2. Model fitting for BSA diffusion in E_PCL

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was 2.71 ± 0.11 g H_2O/g membrane; however after water evaporation the ENf revealed a reversible behaviour with a shrunken conformation. The E_PCL revealed a decrease of average pore size in the range of 30% to 40%, and an average pore diameter of 1/3 of the size when compared to the PCL membrane; this difference is significant enough to influence the transport of larger molecules (e.g. lactoferrin), thru the ENf membrane. The values of *D* acquired by fitting the model, which accounts for both Fickian diffusion and relaxation of polymer [1], of E_PCL were 5.19×10^{-14} m^2/s regarding the BSA migration and 11.25×10^{-14} m^2/s for lysozyme.

Acknowledgements

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STRUCTURAL AND FUNCTIONAL DYNAMICS OF GLIADIN AND GLUTENIN ENRICHED FILMS WITH ADDITIVES

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INTRODUCTION

Bio-based plastics produced from plant polymers e.g. starch and proteins, have potential to replace petroleum-based plastics thereby increasing the economic value of the crops with a positive impact on the environment. Gliadin and glutenin are two protein types of wheat gluten, and are responsible for gluten viscosity and elasticity, respectively. The aim of the present study was to examine the effect of some of the chemical additives (NH_4OH, NaOH and salicylic acid) on mechanical and structural properties of wheat gluten, gliadin and glutenin enriched films.

RESULTS AND DISCUSSION

Additives, such as ammonium hydroxide, is known to enhance the structural and functional properties of gluten based films (Kuktaite et al., 2011), while salicylic acid is known to have free radical scavenging effect and improve barrier properties of gluten-based films. SE-HPLC and RP-HPLC showed that the addition of NH_4OH and salicylic acid increased the molecular weight of gluten polymer, and resulted into increased aggregation and structural rearrangements in all the studied films compared to films without additives. Addition of NH_4OH and salicylic acid in combination increases the number of disulphide bonds and other covalent bonds in gliadin and glutenin enriched films as shown by RP-HPLC results. The addition of NaOH structurally degraded the films probably due to deamidation at high pH resulting in protein chain scission (Olabarrieta et al., 2006).

CONCLUSION

The glutenin enriched films with NH_4OH were most aggregated and showed strong polymerization and protein-protein interactions as compared with all other films tested in this study. The mechanical properties of all bio-based films showed significant improvement in terms of stiffness and tensile strength by the addition NH_4OH and salicylic acid in combination.

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ADVANCED POLYMERIC MATERIALS AND COMPOSITES

CONTENTS

EFFECTS OF CROSSLINKING ON THE PROPERTIES OF CLAY-POLY (VINYL ALCOHOL) NANOCOMPOSITES

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For sustainable and biodegradable paper and paperboard-based packaging to be truly realised the typically used petroleum-derived plastic coatings need to be replaced by suitable alternatives. The alternative products generally have poorer mechanical, barrier and thermal properties and so methods to improve them are sought; the formation of clay-polymer nanocomposites is one viable solution [1].

PVOH/clay based nanocomposites have been developed as environmentally-friendly barrier coatings [2]. These are particularly suited to packaging applications due to their biodegradability and excellent oxygen and aroma barrier properties, but their usage is limited in high relative humidity environments. This study aims to improve the properties of PVOH and PVOH/clay films with respect to water vapour barrier properties, by using crosslinking agents to modify the polymer network.

The extent of crosslinking, using glutaraldehyde, has been carefully controlled by exposing PVOH or PVOH/clay films for increasing periods of time. The crosslinked films have shown significant improvement in water vapour barrier properties (reduction of 70% at 23 °C and 85% relative humidity) and the effect was observable with only short crosslinking times (5 minutes), comparable results were also observed for films treated for 15 minutes and 1-4 hours, but further exposure resulted in a reduction in barrier properties. The extent of crosslinking was monitored using infrared spectroscopy and shown to correlate with the water vapour barrier properties. As a result of crosslinking the swellability of the films decreased and the thermal stability was significantly increased.

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THERMALLY STABILIZED PHBV NANOCOMPOSITES: OBTENTION AND CHARACTERIZATION

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In recent years there has been a growing interest in the development of bioplastics to reduce dependence on oil-based polymers. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), a biodegradable copolyester from the polyhydroxyalkanoate family (PHA), has gained a lot of attention because of its fast biodegradability and biocompatibility as well as a non food-competitive origin. In spite of the significant potential of PHBV to substitute commodity polymers, it still presents a number of properties and processing shortcomings that handicaps their use in many applications, particularly in the food packaging field [1]. These are generally related to a lower mechanical performance (when compared with oil-based polymers) and their low thermal resistance and processing window [2]. An increase in mechanical properties can achieved by incorporating low amounts of nanoparticles [3],such as clays, and the addition of chain extenders can improve thermal stability during melt processing bringing a widening of processing windows [4].

The aim of this study has been to compare the effect of the addition of two nanofillers, a tubular like clay and a laminar clay, on the thermal and mechanical properties of PHBV nanocomposites obtained by melt blending, and to evaluate the influence of the incorporation of a chain extender on thermal stability of nanobiocomposites.

In this work poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV, ENMAT Y1000P Tianan) has been used as base material. The nanofillers used in this work has been halloysite nanotubes (HNT) from NaturalNano and Cloisite® 30B supplied by Southern Clay Products and the chain extender was tris (nonylphenyl) phosphite (TNPP) from Sigma Aldrich.

Full characterization of the composite systems has been developed by means of WAXS, TGA, SEM, TEM and mechanical properties. Morphological characterization reveals a good dispersion of clays in PHBV matrix. Tensile tests show a similar reinforcement in both systems. TGA analysis reveals that the addition of C30B decreases the onset of the thermal degradation (T_{onset}) of PHBV, probably due to the organomodifier, as shown in figure 1.a. HNT, however, increases T_{onset} (Fig. 1.a) and also shifts the maximum degradation temperature (T_d) towards higher temperatures (Fig. 1.b). In all cases the addition of TNPP increased thermal stability (T_{onset} and T_d) being more pronounced in the case of PHBV-HNT-TNPP.

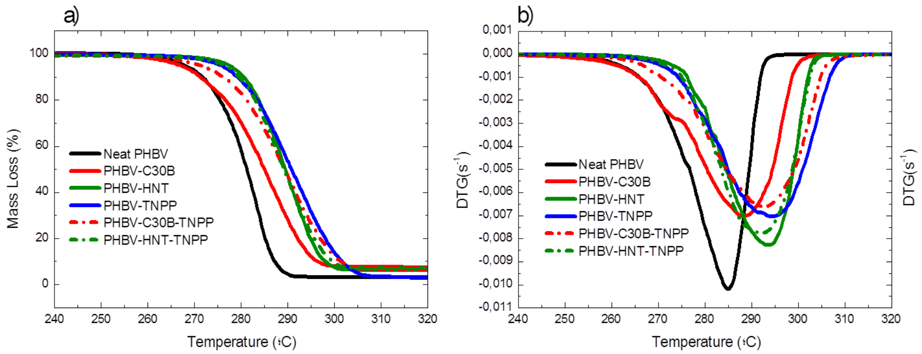

Figure 1. TGA curves of PHBV/clays/chain extender

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CHARACTERIZATION OF POLY (E-CAPROLACTONE)-BASED BIOCOMPOSITES WITH ALMOND AGRICULTURAL RESIDUES FOR PACKAGING APPLICATIONS

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Over the last few years, the increase in the research in bio-composites has been significant. In fact, the worldwide capacity of bio-based polymers is expected to increase from 2.33 MTons by 2013 to 3.45 million MTons in 2020[1]. However, most bio-polymers show relatively poor mechanical and barrier properties and high cost, which currently limit their industrial application[2]. On the other hand, agricultural residues are normally incinerated or dumped causing environmental problems, such as air pollution, soil erosion and decrease in soil biological activity[3]. The use of agricultural residues in bio-composites does not only prevent environmental concerns but can also give farmers a second income source. In this way, this could be an effective and economic method to give added value to an agricultural residue, while reducing the relative high cost of PCL and improving its mechanical properties[4]. The aim of the present work is the study of the effect of the almond skin incorporation to a PCL matrix to get a reinforced low-cost bio-composite. The effects of coupling PCL with the almond skin loading on the thermal, tensile, rheological and barrier properties of bio-composites were investigated.

Formulations of PCL (CAPA^{TM} 6800, M_n=80.000, Perstorp, Sweden) with almond skin residues at 0, 10, 20 and 30 wt% were extruded with a co-rotating twin-screw extruder followed by injection molding. A significant increase in the elastic modulus was observed (462 ± 30 MPa for PCL30 in contrast to 267 ± 12 MPa for neat PCL). As the filler content increased lower elongation at break and impact energy values were obtained, getting more fragile materials with higher Shore D hardness values whereas no significant differences regarding tensile strength values were observed. The addition of almond skin to PCL resulted in continuous phases, as observed by SEM, which was related with modulus improvement. However, the formation of agglomerates at high almond skin concentrations conducted to higher water absorption values. DMA showed a slight increase of the modulus with the T_g value with statistical significant differences between samples in DSC tests. In this sense, as almond skin content increased lower melting and crystallization enthalpies and higher crystallinity degree were observed. Regarding T_g values, some increase took place with the higher reinforcement contents (from -61 ± 1 ºC for neat PCL to -56 ±1 ºC for PCL30). This result can be explained by the mobility of macromolecular chains in the amorphous region and restrictions in the rotational backbone motions of PCL polymer chains through the establishment of hydrogen bonding forces. Finally, TGA results indicated that thermal stability of the material decreased with the fiber contents.

The obtained results suggest that the addition of almond skin natural fibres to a PCL matrix shows a reinforcement effect. These bio-composites could be useful for packaging applications, since better mechanical performance was obtained without significant differences between PCL10 and neat PCL regarding thermal and barrier properties.

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NEW HYBRID POLYESTER - SILANE POWDER COATINGS FOR CORROSION PREVENTION APPLICATIONS

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INTRODUCTION

Corrosion protection by organic coatings is considered one of the most effective and lasting mechanisms to protect galvanised steel. Conventional processes usually require an initial primer or surface pretreatment prior to applying the coating to facilitate adhesion to the substrate [1]; however, this step implies an increase in the cost of corrosion protection as well as environmental problems because in many cases heavy metals are used.

Adhesion promoters based on organosilanes emerged as a new and environmentally safer alternative to replace chromate conversion coating [2], by using as a metal pretreatment [3], or more recently, by directly incorporating on a resin system to obtain a 'superprimer' with outstanding adhesion and corrosion protection properties [4]. In any case, potential anticorrosive properties of these resin-silane combinations are based partly on the improved the adhesion between the coating and the metallic surface. However, directly incorporation of silanes in powder coatings has not yet been studied. In this case, organosilane precursors grafted onto inorganic fillers, as silica particles, seem to be the best alternative to achieve a suitable adhesion promoter additive for powder systems.

RESULTS AND DISCUSSION

A commercial organosilane (alkyl triethoxysilane) grafted on silica particles was directly incorporated at different concentrations as an additive in a polyester powder coating. The coatings formulated were characterised by DSC, adhesion tests and electrochemical impedance spectroscopy (EIS).

Anticorrosive properties of the coatings evaluated by EIS and their adhesion to the substrate were improved with all the formulations containing the adhesion promoter, especially in the coating with 2.5% (Figure 1). The decrease in protection behavior when a certain amount of adhesion promoter content is exceeded can be explained by the presence of agglomerates observed in the morphological study (SEM).

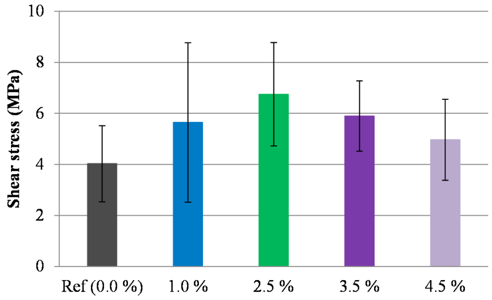

Figure 1.Breaking shear stress of coatings formulated with different amounts of adhesion promoter (ISO 4587:2003)

CONCLUSIONS

The new hybrid polyester-silane coating leads to an improvement in the adhesion and the corrosion protection performance, up to 2.5 wt%. Concentrations beyond 2.5wt % entail the formation of aggregates, which results in a decrease in mechanical and electrochemical properties.

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COMPETITIVE ADSORPTION STUDIES OF POLY (VINYL ALCOHOL) AND PLASTICISERS ON CLAY WITHIN NANOCOMPOSITES

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Clay-polymer nanocomposites are being investigated for use as packaging materials since they offer a unique property profile, which encompasses improved barrier and mechanical properties. Plasticisers are incorporated to help make the barrier coatings more flexible, but can also control or limit the clay dispersion.

The distribution of PVOH and plasticiser in the interlayer of the clay, resulting in part from their competitive adsorption, can play a crucial role in establishing the barrier properties of the coatings. Difficulties in distinguishing whether they were located in the clay interlayer led to this study. Earlier work at Sheffield [1] and the work of Strawhecker and Manias [2] has shown that PVOH exhibited a range of basal spacings depending upon the quantity of the PVOH offered to the clay. Also, quite importantly, at PVOH loadings above 35 wt% diffraction data showed that PVOH expanded the clay more than plasticisers. Consequently, if the plasticiser was preferred over PVOH in this concentration range then some ordering of the system would likely be observed.

A wide experimental matrix covering different clay-polymer-plasticiser compositions and their sequence of mixing have been investigated. Subsequent drying and storage conditions of the composites have also been investigated. The clay investigated was the commercial bentonite, Cloisite Na^+, supplied by Southern Clay Products, whereas the PVOH had a molecular weight (MW) of 30,000. Several plasticisers were investigated, but herein polyethylene glycol with a MW of 600 (PEG600) will be mainly discussed; it represents the middle range in respect of polarity and molecular weight.

The adsorption isotherms of PVOH and/or PEG600 onto Cloisite Na^+ were obtained by using a calibrated thermogravimetric method to determine the amounts remaining in the supernatant after contact with the clay. X-ray diffraction (XRD) traces were collected from composites prepared from aqueous suspensions before centrifugation (BC) and from the sediment obtained after centrifugation (AC) in order to identify whether the polymer or plasticiser was located in the clay interlayer or solution.

Acknowledgement

Ministry of National Education of Indonesian Republic for funding of Khairuddins PhD project through Sebelas Maret University, Surakarta – Indonesia.

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CONTENTS

BIOTECHNOLOGICAL ROUTES FOR THE DESIGN OF NANOSTRUCTURED METAL-BASED ANTIMICROBIAL BIOPOLYMERS

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ABSTRACT

Antimicrobial active packaging is one of the most promising technologies in the food area. Among the most widely used antimicrobials, metals such as silver ions or nanoparticles have emerged as one of the most researched technologies to prevent microbial outbreaks in food contact plastics and surfaces. However, it is known that silver is a rather unstable metal that undergoes colour changes triggered by environmentally-induced reduction and/or agglomeration of this natural biocide. Renewable biopolyesters such as polylactides (PLA) and the microbial polyhydroxyalkanoates (PHA's) are currently either substituting or being assessed to become substitutes of petroleum based plastics such as polyethylene terephthalate (PET). The first overall aim of this work was to develop biotechnological methods for the *in situ* synthesis of stabilized silver nanoparticles (AgNP) within microbial cheese whey derived PHA to render high antimicrobial materials with higher silver stability. The second aim of this study was to incorporate an alternative metal compound, i.e. zinc, on PLA by the solvent casting technology and compare the stability, morphology and biocide capacity of the obtained films. These technologies are currently also being implemented *in situ* during PHA's production.

MAKING FLEXIBLE MAGNETIC AEROGELS AND STIFF MAGNETIC NANOPAPER USING CELLULOSE NANOFIBRILS AS TEMPLATES

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ABSTRACT

Nanostructured biological materials inspire the creation of materials with tunable mechanical properties. Strong cellulose nanofibers from bacteria or wood can form ductile or tough networks that are suitable as functional materials. Here, we show that freeze-dried bacterial cellulose nanofibers aerogels can be used as templates for making lightweight porous magnetic aerogels, which can be compacted into a stiff magnetic nanopaper. The ca. 40 nm thick cellulose nanofibers act as templates for the non-agglomerated growth of ferromagnetic ferrite nanoparticles, diameter: 40–120 nm. Unlike solvent-swollen gels and ferrogels, the magnetic aerogel is dry, lightweight, porous (98%), flexible, and can be actuated by a small household magnet. It can also absorb water and release it upon compression and due to their flexibility, high porosity and surface area; they are expected to be useful in microfluidics devices and as electronic actuators. Further, similar template reactions are demonstrated on wood cellulose fibers, and a concept loudspeaker without any moving electrical parts is demonstrated.

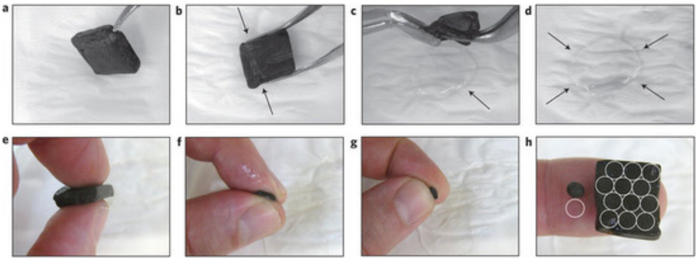

Figure 1. a–d, Magnetic aerogel (dimensions 10 mm × 10 mm × 3 mm) with ~0.3 cm^3 absorbed water content (a) can be compressed (arrows in b) by a pair of tweezers. More than 95% of the water content (shown by arrows) is released upon compression (c–h)

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CONTENTS

NEW ZINC-BINDING POLYMERIC MATERIALS FOR APPLICATION IN ORGANIC SOLAR CELLS

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Solar cells made of plastics (also known as organic solar cells, OSCs) are of major interest nowadays being a promising alternative to fossil fuels due to their low manufacturing cost and attractive end-user qualities like easy installation and maintenance. However, they still have low efficiencies compared with other solar energy harvesting technologies (particularly silicon-based devices[1]). Moreover, the stability of the plastic devices is limited by various processes that occur during routine usage – oxidation, photodegeneration, phase segregation, delamination, etc.[2] New polymers are introduced to solve these problems, leading to longer life-times of plastic solar cells.

This work reports an efficient method to synthesise new zinc-binding polymers for various organic electronics applications. Polymers of 3,4-dimethoxystyrene are obtained by a facile procedure of reversible addition−fragmentation chain-transfer polymerisation (RAFT). RAFT polymerisation results in well-defined polymers over a range of molecular weights with low polydispersities. Different chain transfer agents (CTAs), synthesised from commercially available materials, allow simultaneous end chain functionalisation of the polymers. Poly(3,4-dimethoxystyrene) is subsequently treated to yield poly(3,4-dihydroxystyrene) with higher zinc-binding capacity than the parent polymer. Both polymers are characterised for their processing properties. Zinc oxide binding capacities are measured by Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDXA). Coupling of poly(3,4-dimethoxystyrene) and poly (3,4-dihydroxystyrene) to a single molecule fullerene C60 is subsequently discussed in this work for the fabrication of completely new materials for organic optoelectronic devices.

Acknowledgements

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MAGNETICALLY RESPONSIVE ELECTROSPUN NANOFIBRES

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Electrospinning can be used to prepare magnetic nanocomposite fibers. In principle, several basic strategies can be used, e.g.:

- electrospinning of a polymer solution containing magnetic nanoparticles (diameters around 10 nm)
- in situ synthesis of iron oxide nanoparticles in appropriate nanofibers through an electrospinning process (e.g., polymer solution having Fe2+ and Fe3+ ions in a gaseous ammonia atmosphere)
- electrospinning of appropriate nanofibres, followed by a postmagnetization procedure leading to the attachment of magnetic nanoparticles to the outer surface of nanofibres
- Electrospinning of magnetic-nanoparticle-doped polymers under the influence of a magnetic field producing aligned arrays of fibers over large areas

Magnetically responsive nanofibres may have several interesting applications in the future, such as a microwave heating material in MHz frequency range, a possible ultra-lightweight microwave absorbing material in GHz frequency range, preparation of special filtration materials, drug release systems, immobilization of enzymes, antibodies, or other biologically active compounds etc.

CHARACTERIZATION, STABILITY AND KINETICS OF CAFFEINE RELEASE OF Β-LACTOGLOBULIN NANOPARTICLES

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INTRODUCTION

Addition of bioactive compounds into food matrices could adversely affect the food flavour and texture (Giroux et al. 2010) also the incorporation of very hydrophobic bioactives into clear and non-fat semi-solid or liquid foodspossess a technical difficulty (Li et al. 2012). Protein based micro and nanoparticles have been investigated for the protection and delivery of sensitive bioactive compounds that are prone to degradation during food processing, storage and/or digestion (Giroux et al. 2010). β-lactoglobulin (β-Lg) the major whey protein has very good gelling properties and can produce nanoparticles that can be used as nanovehicles for nutraceutical products (Zimet & Livney 2010). The aim of this study is to investigate the production (based on aggregation properties of β-Lg), characterization (in terms of size by Dynamic Light Scattering technique and by electron microscopy) and stabilization of β-Lg nanoparticles used to controlled release of encapsulated caffeine.

RESULTS AND DISCUSSION

β-Lactoglobulin (β-Lg) nanoparticles were prepared at the isoelectric point of the protein (pH =5.5), at varying protein concentrations (0.2%, 0.5 % and 1%) and by inducing heat denaturation at 65 and 75°C for 15 minutes. Aggregation was stopped by cooling the dispersions in ice. Yield of aggregation was determined by filtering dispersions thorough a 50 kDA ultrafiltration membrane and determining the non-aggregated fraction of protein in the permeate. Nanoparticles size was determined by dynamic light scattering and ranged between 140 to 220 nm in diameter. Size increased with protein concentration. At 65 °C it was found that aggregation was not completed.

β-Lactoglobulin (β-Lg) nanoparticles were used as a protective encapsulant against adverse environmental conditions and for the controlled release of caffeine. Maximum entrapment efficiency of 40% was obtained at 1:10 caffeine: β-Lg molar ratio. Partial degradation of the structure of the β-Lg nanoparticles loaded with caffeine was observed when incubated in a simulating gastric fluid containing pepsin for 10 min at 37°C and pH 1.5 at protein:enzyme ratio 3:1 w/w based on measurements of particle size by dynamic light scattering. After 120 minutes incubation 64% reduction in particle size was observed whilst only 22 %

of caffeine was released which suggests that the degraded nanoparticles retain their encapsulating properties under these conditions.

The kinetics of β-Lg nanoparticles degradation fitted a hyperbolic shape model which enabled to estimate the minimum aggregate size upon complete degradation. On the other hand, caffeine was released from the β-Lg nanoparticles following a linear kinetic consequently, particle size does not determine caffeine release. However a good fitting was found between caffeine release and area to volume ratio suggesting that the latter is a key factor in the release of caffeine.

CONCLUSION

Overall it can be concluded that β-Lg nanoparticles could be used for the effective controlled release of caffeine.

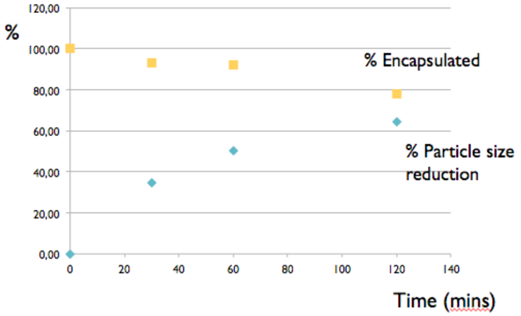

Figure 1. Particle degradation and caffeine release at simulating stomach conditions (pH=1.5, pepsin, at 37 ˚C,10 mins).

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MELT POLYCONDENSATION TO IMPROVE THE DISPERSION OF BACTERIAL CELLULOSE INTO POLYLACTIDE VIA MELT COMPOUNDING. ENHANCING BARRIER AND MECHANICAL PROPERTIES

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ABSTRACT

Bacterial cellulose nanowhiskers (BCNW) were incorporated into polylactide (PLA)-based composites. With the aim of improving the BNCW dispersion in the final material and prior to melt blending for processing the materials, lactic acid oligomers (OLLA) were chemically grafted onto the surface of BCNW through a melt polycondensation reaction. This in-situ polymerization reaction enhanced the compatibilization between hydrophilic cellulose and hydrophobic PLA.

The optimized dispersion of the BCNW in the nanocomposites was confirmed when compared to the direct melt mixing of the freeze-dried BCNW or partially hydrated BCNW. After melt polycondensation, PLA-based nanocomposites were prepared by melt compounding. In order to study the effect of BCNW in the final properties of the nanocomposites, the amount of OLLA was kept constant and a reference material was prepared containing the same amount of free oligomer. Thermal properties were determined using diferential scanning calorimetry (DSC). DSC revealed that, although cellulose content did not affect the melting temperatures, crystallinity as reflected by enthalpy values was significantly diferent. Furthermore, differences between grafted and ungrafted oligomers on melting temperatures was noticed. The mechanical properties showed an improvement in elastic modulus and tensile strength, up to 52% and 31% respectively. This was mainly ascribed to the promotion of filler-filler and filler-matrix interactions. Moreover, the developed nanocomposites showed a reduction in the water and oxygen permeability (measured at 80% RH) reaching improvements up to 15 % and 21%, respectively. This could be explained by well-dispersed nanocrystals acting as blocking agents within the polymeric matrix, reducing the diffusion through the nanocomposite films and, hence, the water and oxygen permeability. Therefore, this work offers a new route for incorporating well dispersed cellulose nanowhiskers within a hydrophobic polymer matrix, overcoming the dispersion problems that this entails. At the same time the development of the materials has been performed using a technique widely used industrially.

CONTENTS

ELECTROSPUN NANOFIBROUS WEBS INCORPORATING ANTIOXIDANTS FOR FOOD PACKAGING

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Electrospinning is a convenient and efficient method generally operating at room temperature to produce nanofibers [1-3]. During the electrospinning process a polymeric liquid that is exposed to electrostatic field being provided from power supply is continuously drawn and deposits randomly on the collector; and the nanofibers are obtained with the evaporation of the solvent [3]. The unique properties like high surface area to volume ratio, highly porous structure and design flexibility enable electrospun nanofibers to be used for several applications including wound dressing, tissue scaffold, drug delivery, food packaging, filtration, energy, catalysis, sensors, etc[1-3]. In addition, owing to the room temperature and ambient process conditions that provide protection for the bioactive compounds in electrospun nanofibers, electrospinning is used for production of functional nanofibers containing active agents like drugs, antioxidants, flavors/fragrances and antibacterial agents.

Cyclodextrins (CDs), cyclic oligosaccharides, consist of 6 (α-cyclodextrin, α-CD), 7 (β-cyclodextrin, β-CD) or 8 (γ-cyclodextrin, γ-CD) glucopyranose units, and they are bound together by α-(1-4) linkages forming a truncated-cone shaped structure [4]. Owing to their polar hydrophilic outer shell and relatively hydrophobic cavity, CDs are known for their ability to build up host–guest complexes with several kinds of guest molecules according to the polarity and size. The formation of inclusion complex (IC) leads to considerable changes in the solubility and reactivity of the guest molecules [5]. Owing to the IC between CDs and guest molecules, many improvements can be achieved such as controlled release, enhancing solubility, bioavailability and chemical stability of poorly soluble active agents; increasing thermal stability of volatile agents. Therefore, CDs are used in cosmetic, pharmaceutical, food and environmental protection industries. Moreover, it is quite applicable to incorporate CD-IC with electrospun nanofibers to provide properties of both CDs and electrospun nanofibers.

α-Tocopherol (α-TC) and quercetin (QU) are widely used antioxidants for food packaging applications. However, usage of α-TC and QU has been limited since they are poorly soluble compounds in aqueous solution. On the other hand, CDs which are known to have capability to form host-guest IC with several kinds of molecules and to improve the stability of guest molecules against to various impacts [5]. Therefore, IC of α-TC and QU with γ-CD (α-TC/γ-CD-IC and QU/γ-CD-IC) in which the molar ratio of α-TC and γ-CD is 2:1 and QU and γ-CD is 1:1 were prepared. We used polylactic acid (PLA) and zein as carrier polymer matrixes; PLA nanofibers incorporating α-TC/γ-CD-IC (PLA/α-TC/γ-CD-IC-NF) and zein nanofibers incorporating QU/γ-CD-IC (zein/QU/γ-CD-IC-NF) were produced via electrospinning technique. For reference, PLA nanofibers incorporating free α-TC without CD-IC (PLA/α-TC-NF) and zein nanofibers incorporating free QU without CD-IC (zein/QU-NF) were also produced. X-ray diffraction proved the formation of CD-IC with the characteristic channel peaks of γ-CD. The stoichiometry of α-TC and γ-CD was determined as 2:1; whereas the stoichiometry of QU and γ-CD was determined as 0.89:1.00 by using nuclear magnetic resonance. Scanning electron microscopy images of nanofibers showed that incorporation of antioxidants and CD-IC of antioxidants did not change the fibrous morphology of nanofibers. PLA/α-TC/γ-CD-IC-NF and PLA/α-TC-NF exhibited 93.27 % and 92.91 % antioxidant activity; while zein/QU/γ-CD-IC-NF and zein/QU-NF had 90.40 % and 84.08 % antioxidant activity, respectively. The antioxidant activity results showed that electrospinning has no negative effect in the antioxidant activity of α-TC and QU. Moreover, the slower release rate and higher release amount of α-TC into 95 % ethanol from PLA/α-TC/γ-CD-IC-NF compared to PLA/α-TC-NF is most likely due to the presence of α-TC/γ-CD-IC. Since CD-IC causes lower diffusion rate arising from the increment in the molecular weight of guest molecules; improvement in the solubility of guest molecules and protection against various impacts. As a conclusion, these nanofibers have potential to be used as food packaging materials.

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MOLECULARLY IMPRINTED POLYMERS FOR RAPID FISH FRESHNESS DETERMINATION

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INTRODUCTION

Freshness is one of the main attributes of quality for commercialization and consumption of fish and plays an important role in human health. Nucleosides degradation and related compounds have been shown to be a good quality index to control freshness of fish during handling and processing[1].

Molecularly imprinted polymers (MIPs) are stable polymers with molecular recognition abilities, provided by the presence of a template during their synthesis and thus are excellent materials to provide selectivity to sample preparation[2]. MIPs could be used as selective absorbent materials for the clean-up and preconcentration of substances from complex matrices such as foodstuffs, before the separation procedures commonly used for their determination. The application of MIPs, as a solid phase extraction (SPE) sorbents for the selective preconcentration and clean-up of nucleosides could be of great interest to the food industry for the determination of fish freshness.

The aim of this study consists in the application of moleculary imprinted polymer-solid-phase extraction (MIP-SPE) for the selective extraction, clean-up and pre-concentration of inosine and hypoxanthine from hake muscle.

RESULTS AND DISCUSSION

In this study, the method for the selective preconcentration of hypoxanthine and inosine in hake samples was validated using different MIP-SPE and compared to results obtained with a traditional method of extraction. The methodology of extraction consists in incorporating the sample of hake with MIP and then carried on as in a solid-phase extraction. SPE tubes were packed with the prepared mixture of MIP-sample and after washing with hexane, the substances are eluted with 25% ammonium hydroxide. To improve chromatographic resolution, the pH was adjusted to 9. The nucleosides were successfully separated, identified and quantified by high performance liquid chromatography coupled to a photodiode array detector (HPLC-DAD). The calibration curves were prepared for each substance ($r^2 > 0.9999$ for both molecules) and the linearity response was evaluated in samples spiked with different concentrations of each substance (500 - 2000 mg/kg).

The results showed that using the traditional method both the linearity and recovery rates are high for the substances under study (> 84% for hypoxanthine and 100% for inosine). Using the MIP-SPE extraction method, although the analysis time is shorter than traditional method, the results obtained showed that samples spiked with lower concentrations of nucleosides exhibit lower recovery values than the traditional method. Using one of the MIPs evaluated recoveries up to 84.6% were obtained for inosine.

CONCLUSION

MIPs showed good selectivity toward inosine and therefore suitable for the application, offer the advantages of selectivity, enabling an effective sample pretreatment of complex matrices such as foodstuffs and simplifies subsequent chromatographic analysis.

Acknowledgements

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USE OF ELECROSPUN HYDROCOLLOIDS ADHESIVE INTERLAYER TO ENHANCE BARRIER PROPERTIES OF BIOPOLYESTERS

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In the food packaging area, the most commercially viable materials at the moment are some biodegradable polyesters (such as polylactic acid -PLA- or polyhydroxyalkanoates-PHA-), which can be processed by conventional equipment. In fact, these materials are already used in a number of monolayer and also multilayer applications in the food packaging field. In our research group, we have developed high oxygen and vapour barrier multilayer structures by combining layers of PHA with layers based on proteins and polysaccharides which were obtained by the electrospinning process. Electrospinning is a simple, versatile and efficient method to produce high-performance polymeric fibres with diameters ranging from the micro to the nanoscale[1]. This technique relies on electrostatic force to draw polymer solution or melt into ultrathin fibres, which can be deposited as fibrous mats for many potential applications.

Although, one of the most important problems is the adhesion of layers made of various incompatible materials (such as PHA and hydrocolloids), the incorporation of electrospun zein or pullulan nanofibers as interlayers showed good adhesion between layers. Furthermore, this technique generates high oxygen barrier structures even at high relative humidity [2,3].

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DEVELOPMENT OF HEAT MANAGEMENT MATERIALS OF INTEREST IN FOOD PACKAGING

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The use of latent heat storage systems using phase change materials (PCMs) is an effective way of buffering thermal fluctuations and has the advantages of high-energy storage density and the isothermal nature of the storage process. Direct applications of PCM´s is difficult since they have weak thermal stability, low thermal conductivity and some of them are liquid at ambient temperature and, thus, are not easy to handle or to be directly incorporated into packaging structures and refrigeration equipments. Therefore, the encapsulation of the PCM in a shell material is a plausible solution to avoid all these problems. One technique increasingly being used for the microencapsulation of materials is electrospinning. This technique has proven to be a suitable method for encapsulation of several components, including biomedical substances, functional food ingredients, PCM´s and others substances within polymer matrices. The aim of this work was to develop heat management materials based on the encapsulation of a PCM which melts at 5ºC (RT5 - core material) inside two different polymeric matrices (polycaprolactone –PCL- and polystyrene –PS-) (shell material) by means of the electrospinning technique. Results showed that PCL/PCM slabs were able to encapsulate a greater amount of the RT5 than those obtained with PS. These hybrid structures can be of great interest as energy storage systems to advantageously protect sensitive products in packaging or refrigeration equipments.

NAFION/POLYANILINE COMPOSITE MEMBRANES SPECIFICALLY DESIGNED TO REDUCE METHANOL PERMEABILITY

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Direct methanol fuel cells (DMFC) using polymer electrolyte membranes are a promising alternative for future energy needs combined with cleaner environment, because they do not require any fuel processing equipment and can be operated at relatively low temperatures[1]. However, commercialization of the DMFC is limited by two major technical problems: (i) slow methanol oxidation kinetics of the anode catalyst and (ii) methanol diffusion from anode to the cathode side, across the polymer electrolyte membrane. The methanol crossover causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning[2]. Nowadays, perfluorinated membranes are extensively studied for their applications in fuel cells, particularly, for direct methanol fuel cells. To date, Nafion is still the most performing cation exchange membrane. However, some progress is still needed in order to enhance the membrane performance in terms of reduce the loss of fuel (methanol) across the polymer electrolyte membrane. Nafion has also been modified with conducting polymers such as poly(aniline) (PANI)[3] to reduce the methanol crossover in direct methanol fuel cell applications. Nevertheless, very few works have been reported in the literature on Nafion-PANI composite membranes.

Within this context, the scope of this work is to study the modification of Nafion NR-212 membrane by in situ chemical polymerization of aniline using two different methods: immersion and crossover. These Nafion-PANI membranes have been extensively characterized in order to understand how the microstructure of this composite membrane affects the methanol crossover and the electrochemical performance in DMFC applications.

Commercial Nafion membrane NR-212 was purchased by Dupont. Aniline was purchased from Sigma Aldrich and was used as received. The composite membranes obtained by immersion modification were prepared according to the procedure suggested by Fabrizio et al [4]. The crossover modification procedure suggested in this work is based in the one proposed by Munar et al. [5]. The polymerization exposure times were 1, 2 and 5 hours for immersion and 2 and 4 for crossover method. The membranes prepared were identified with the following code: Naf-S-Y and Naf-C-Y, where S stands for immersion modification, C stands for immersion modification and Y is the polymerization time, in hours.

Results show that no reduction in membrane permeability was observed by immersion modification of the membrane (Table 1). This method of modification, therefore, cannot be considered as a viable alternative to untreated Nafion. On the other hand, the permeability tests for membranes modified by crossover show a remarkable improvement in methanol crossover resistance through the membrane (Table 1). This decrease in permeability is thought to be mainly due to polymerization of aniline inside the ionic domains of Nafion. The PANI would partially block the pathway to ion transport, thus entailing a reduction in proton exchange capacity, which affects the performance of DMFC (Table 2).

Sample	**Apparent methanol permeability coefficient ($\mathrm{cm^2/s}$)**	
	Room temperature	**T^a = 70ºC**
Nafion	$2,40\cdot10^{-7}$	$9,45\cdot10^{-7}$
Naf-S-1	$3,67\cdot10^{-7}$	$7,91\cdot10^{-7}$
Naf-S-2	$2,51\cdot10^{-7}$	$1,17\cdot10^{-6}$
Naf-S-5	$2,82\cdot10^{-7}$	$9,52\cdot10^{-7}$
Naf-C-2	$1,87\cdot10^{-7}$	$7,25\cdot10^{-7}$
Naf-C-4	$1,26\cdot10^{-7}$	$5,65\cdot10^{-7}$

Table 1. Apparent methanol permeability coefficient at different temperatures for Nafion-PANI modified membranes.

Sample	**Pf (mW/cm^2)**		
	T^a = 40ºC	**T^a = 60ºC**	**T^a = 80ºC**
Nafion	54	73	87
Naf-S-1	45	62	80
Naf-S-2	32	45	59
Naf-C-2	20	25	49

Table 2. Power density at different temperatures for Nafion-PANI modified membranes

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BIODEGRADABLE POLYMERS, BIOPOLYMERS AND BIOMATERIALS

CONTENTS

ECO – BIODEGRADABLE COMPOSITES WITH APPLICATIONS IN THE REPLACEMENT OF PROTECTION PACKAGES FROM EPS

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ABSTRACT

The poster relates the modalities and mechanisms for decrease of environment pollution –ENVIRONMENT FRIENDLY PRODUCTS (green chemistry).

At the moment, around 40% of EPS total production –especially that from packaging industry– has a short life cycle, found as waste, and over 50% of them go to cesspools. From specialists' estimations, around 90% of total volume of plastics unrecycled waste is represented by waste from EPS. It can be said that finding environment friendly technological alternatives, for the purpose of EPS production and recycling, represents an important target for any research.

In these conditions, an alternative to obtaining, using and recycling of EPS materials is represented by usage of biodegradable materials that exist in nature to create a new category of materials, with a similar behaviour to plastics on the duration of their usage and that at the end of life cycle are 100% biodegradable.

THE MAIN IDEA IS TO REPLACE EPS MATERIALS WITH AN ALTERNATIVE COMPOST MADE OF VEGETAL AND BIOMATERIAL WASTES

The system propose through this project functions like this: mycelium is instilled into a vegetal compost rich in lignin that is introduced in a completely closed cast matrix. Here, mycelium will develop until it becomes a solid product with properties similar to EPS, then the growth process is blocked through thermal treatment. Resulting product, for example, a protection package, once arrived at client can be used again as fertilizing compost for gardens – this type of material becomes a nutrient in agriculture.

The project's solution supposes: usage of organic raw materials that are not used for food, without significant economical value, in conditions of a technology where the process doesn't take place in equipment's that use energy, but practically, the used living organisms are developing using raw material (lignin) from inside the system, similar to the process in nature.

This project proposes a novel solution, at least at national or European level, through obtaining and usage of a biocomposite obtained from a mushroom mycelium and a sublayer of mushroom growth and development that has the role of biocomposite filling mass.

Also, the biotechnological method of obtaining this biocomposite is original, with special qualities regarding biodegradability.

Another dimension of this project’s novelty results from the fact that the obtaining procedure of proposed biocomposite uses natural materials ‘’green”, meaning vegetal products waste. Their usage ensures environment’s sanitation through exploitation of materials with value of draft. At the same time, ‘’the ecological spirit” of the whole action and project is continued in the phase of using biocomposite in package industry that are 100% ecological, meaning they are clean (without a risk of chemical pollution), and also in the package recycling phase, meaning that after their usage, through the fact that they are biodegradable and can be used as fertilising product for soil in agricultural production or as an addition or suplement to materials used for obtaining recommended organic composts for agricultural crops fertilization.

CONTENTS

ECO-EFFICIENT, BIODEGRADABLE AND TAILORMADE BIOCOMPOSITES FROM PHBV AND WHEAT STRAW FIBERS

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Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a bacterial polymer that constitutes a promising alternative to petrosourced polymers, due to their good barrier properties, full biodegradability and potential biosourcing. Still expensive, PHBV could be associated with lignocellulosic fibers to produce composite materials with a decreased final cost and modulated functional properties. Among the lignocellulosic biomass, wheat straw, which is an abundant, renewable and low-cost by-product of the wheat industries, can be fractioned using dry-processes in order to generate micrometric fibers with specific size and surface reactivity. Lignocellulosic fibers, which are hydrophilic, usually present a low affinity with apolar polymers, leading to the formation of fiber aggregates and a poor fiber/matrix interfacial adhesion. To ensure the improvement of the final properties of the biocomposites, the control and understanding of the fiber/matrix interface is required. The objective of the present work, carried out in the framework of the European project EcoBioCAP (FP7-KBBE-2010-4 - http://www.ecobiocap.eu/), is to decipher how it is possible to develop low-cost, eco-efficient and biodegradable biocomposites from PHBV and wheat straw fibers (WSF) for food packaging. It will focus on the role of the fiber/matrix interface in the structure/properties relationships.

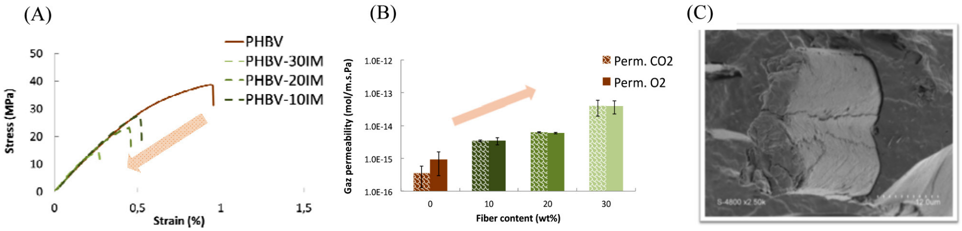

Figure 1. (A) Stress *vs*. strain typical curves of PHBV/WSF composites for increasing fiber content; (B) CO_2 and O_2 permeabilities in PHBV/WSF composites as a function of fiber content; (C) Scanning electron microscopy picture of a cryo-fractured surface of PHBV/WSF composite (evidence of fiber pull-out)

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PHBV/WSF biocomposites were successfully processed to obtain trays. It was shown that increasing fiber content led to a more difficult processability (whereas being interesting regarding composite cost reduction), a degradation of the mechanical properties as regards to the polymer alone (Fig.1A), and an increase in gas (water vapour, O_2 and CO_2) permeability (Fig. 1B). Since no significant change in crystallinity was observed in the presence of fibers, these results were ascribed to a polymer thermal degradation and overall, to a poor fiber/matrix adhesion (Fig. 1C) preventing an efficient stress transfer at the fiber/matrix interface and allowing to create the preferential percolating pathway between hydrophilic fibers for the diffusion of gases. The increase in gas permeability opens new windows of applications for such biocomposites, especially for the packaging of respiring food products. The plasticization strategy was investigated to overcome the breakability of PHBV/WSF composites. A screening of different plasticizers allowed to identify a citric acid ester as the best plasticizer for PHBV. The introduction of 10wt% of this plasticizer resulted in an elongation increase of a factor 3. This plasticizing effect was conserved in the case of reinforcement with WSF, which is favorable for further sustainable applications.

PHBV/MICROCELULLOSE COMPOSITES: CHARACTERIZATION AND BIODEGRADATION IN COMPOSTING CONDITIONS

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Interest in bioplastics for commodity markets, especially packaging, has grown at a rapid rate over the past several years. There are attractions from an industry and societal viewpoint in using renewable polymers derived from non-petroleum sources and biodegradability is also an important factor in light of growing concerns about plastic wastes in the environment [1]. Biodegradation in composting conditions of plastic packages seems to be one of the most promising solutions to the plastic waste management due to the difficulty in separating the plastic package from the organic residues.

Most of the biopolymers suitable for its use in packaging applications have either poor properties or high cost when compared with the commodity oil-based products. A possible solution for these handicaps is to develop composites with fillers. The fillers may decrease the price at high loadings but this may also decrease performance of final material and can even hinder the biodegradation rate when composting.

In this study poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV, ENMAT Y1000P Tianan), a biodegradable copolyester from the polyhydroxyalkanoate family (PHA), which has gained a lot of attention because of its fast biodegradability and biocompatibility as well as a non food-competitive origin, has been used as base material. The filler used in this work has been microcellulose (TC90) from Creafill.

For the present work, composites containing 3, 10, 25, and 45wt% cellulose have been obtained by melt blending in an internal mixer. Full characterization of the composite systems has been developed by means of WAXS, TGA, DSC, SEM, DMA and mechanical properties. Results show that for high cellulose loadings the microfibers have a reinforcing effect.

Biodegradability of the composites in composting conditions was studied. For so, a lab-scale composting plant has been built according to international standards[2] and biodegradation under moisture and oxygen controlled conditions has been monitored for over six weeks. The results show an increase in biodegradation rate for the composites compared to the neat polymer. This increase has found to be over 20% for the sample containing 25wt% cellulose.

This work shows that filling PHBV with microcellulose can lead to composites with improved mechanical performance and biodegradability, together with a decrease in the cost of the final material.

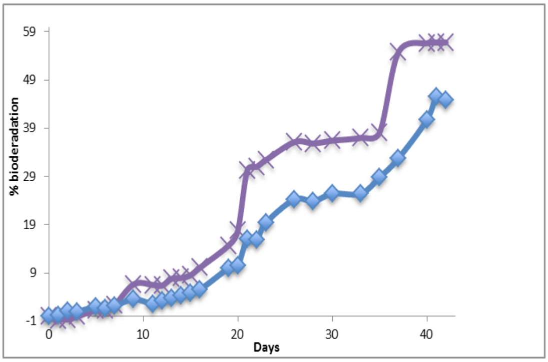

Figure 1. % of biodegradation over the 6 weeks for the neat PHBV (blue) and the sample containing 25% of cellulose (purple).

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BIO-BASED PET COPOLYESTERS FROM A D-MANNITOL-DERIVED BICYCLIC DIOL

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INTRODUCTION

Poly(ethylene terephthalate) (PET) is a linear aromatic polyester of exceptional importance for its large number of applications in a wide variety of domestic, industrial and technological fields.[1] PET displays an excellent pattern of basic properties such as high mechanical strength, good thermal stability and low permeability to gases in addition to an exceptional transparency. Nevertheless, there is currently a growing interest in increasing the glass transition temperature (T_g) of PET to extend its use to new demanding applications such as the hot-filled and pasteurized-container fields.[2] Also great efforts are being made nowadays to incorporate renewable and degradable units into PET.[3]

EXPERIMENTAL

The carbohydrate-based bicyclic diol 2,4:3,5-di-*O*-methylene-D-mannitol (Manx) was synthesized following the procedure recently reported by Lavilla et. al.[4] PE_xManx_yT copolyesters were obtained from a mixture of ethylene glycol, Manx and dimethyl terephthalate with the selected composition, as depicted in Figure 1.

RESULTS AND DISCUSSION

Random PE_xManx_yT copolyesters covering the whole range of molar compositions were obtained. The copolyesters had M_w in the 33,000-41,000 g·mol^{-1} interval and were thermally stable up to nearly 380 ºC.

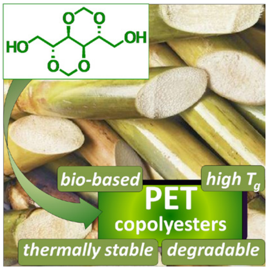

Figure 1. Synthesis of the bio-based PET copolyesters

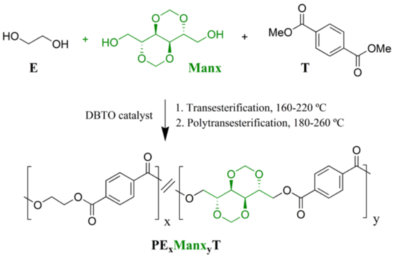

Figure 2. Main features of the bio-based PET coppolyesters

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The DSC analyses revealed that the incorporation of Manx units in the chain of PET induced a significant increase in the glass-transition temperature of the polyester. The T_g steadily increased as ethylene glycol was replaced by Manx units going from 81 ºC for PET up to 130 ºC for $PE_{15}Manx_{85}T$ copolyester. These results are fully consistent with the T_g value of 137 ºC observed for the PManxT homopolyester provided that the microstructure of the copolyesters is at random. Copolyesters containing minor amounts of Manx were semicrystalline whereas those with contents equal or more than 30% of Manx were amorphous. Stress-strain parameters were affected by composition, increasing tensile strength and elastic modulus and reducing elongation at break when introducing Manx units. These bio-based PET copolyesters showed enhanced susceptibility to hydrolysis.

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APPLICATIONS OF ELECTROSPINNING OF BIOPOLYMERS IN THE FOOD AND FOOD PACKAGING AREAS

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Looking genuinely at nature, nanofibers often serve as a basic platform where either organic or inorganic components are built upon. For instance, cellulose nanofibers would represent the building block in plants while collagen nanofibers in the animal body. The fiber structure exhibits, from a structural view point, the ability to transmit forces along its length and generate barrier properties against the transport of low molecular weight components. To follow this extraordinary nature's design, technologies able to fabricate nanostructured fibers from a variety of materials and mixtures is an indispensable pre-requisite. Control over the nanofibers arrangement, size, composition and morphology is also necessary to optimize such structural requirements.

Electrospinning is a physical process used for the formation of ultrathin fibers by subjecting a polymer solution to high electric fields. At a critical high voltage (5-35 kV), the polymer solution droplets distort and forms the so-called cone of Taylor that erupts from the solution to form a charged polymer jet. This stretches and is accelerated by the electrical field towards a grounded and oppositely-charged collector. As the electrospun jet travels through the electrical field, the solvent completely evaporates while the entanglements of the polymer chains prevent it from breaking up. This results in the generation of highly functional and flexible ultrathin polymer fibers in the form of non-woven mats. In this area, our group have recently developed high throughput equipment based in a multinozzle coaxial technology that allows high productivity of fibers.

The current paper will present innovative advances carried out within our research group in which various applications of the high voltage spinning processing technique making use of biopolymers and biopolymeric blends will be reviewed (1-10). These include examples in which new antimicrobial nanostructured fiber mats with strong biocide efficiency were successfully developed, as well as nanoencapsulates of active and bioactive food ingredients, nanostructured temperature buffers with heat storage capacity and high barrier nanobiocomposites and nanolayers of interest in food packaging applications.

Acknowledgements

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ACTIVE PACKAGING STRATEGIES BASED ON SILVER ION RELEASING BIOPOLYMERS

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Although application of silver based antimicrobial systems is a widespread technology [1], its implementation in areas such as food packaging is still challenging due to the instability issues affecting speciation and bioavailability of silver ions, and migration restrictions to foodstuffs in some legal frameworks [2-3]. In the present work, silver ions, not nanoparticles, were directly incorporated into biopolymers, such as ethylene vinyl alcohol copolymer (EVOH) and polylactide (PLA) matrices, both by casting or melt-compounding techniques. The release and speciation of silver ions from the polymer matrices to liquid or solid environments was monitored over time and correlated with the physicochemical characteristics of the polymer and its antimicrobial performance. Under optimum conditions, silver ions were found to be outstandingly effective even at the nanomolar level. The sorption induced release of silver ions from EVOH matrices was found to be faster and less sustained than in PLA [4-5]. Surface release in contact with moisture was shown to be about ten times lower than when immersed in liquid media. However, the effectiveness by surface contact was significantly higher than in liquid food samples. Application of a functional barrier with beeswax to PLA further aided in tuning the release profiles as to produce a sustained release of silver ions under different conditions throughout a week exposure. The results give new insight into the production of antimicrobial polymers based on the release of ionic silver and about their potential application in antimicrobial food packaging.

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IMPROVING THE STABILITY OF GUT HEALTH PROMOTING FUNCTIONAL INGREDIENTS BY INNOVATIVE ENCAPSULATION TECHNOLOGIES

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The immobilization by encapsulation of functional and added-value components is an area of great interest in the design of fortified foods or as in novel bioactive packaging strategies(1,2). The main aim of encapsulation in the food area is to protect sensitive food components from moisture, oxidation, heat or extreme conditions during processing, or to mask component attributes, as undesirable flavours.

The most common encapsulation techniques involve the use of high temperatures or organic agents, leading to some destruction of sensitive encapsulated nutrients as well as toxicity problems associated with residual organic agents (3). This study reports on a novel encapsulating technology based on a proprietary electrohydrodynamic processing for the stabilization and shelf life extension of added-value food ingredients that do not involve severe conditions, both in terms of temperature and solvents used, and that gives rise to controlled micron, submicron or nanometric capsule sizes (4,5,6,7,8,9). Here, through three different case studies we show the tremendous potential of this processing tech in the food science area for development of novel functional ingredients (5,7,8,9).

In the first case study (7) we demonstrate the strong stability against UV light of an encapsulated bioactive antioxidant, i.e. β-carotene, compared to the stability of the non-encapsulated β-carotene reference samples. This compound is commonly used as a dietary supplement for its function as provitamin A and as a natural antioxidant, and as food colorant in margarines and fruit juices. But carotene and the other carotenoids are oxidized by light and heat exposure during food processing due to the presence of conjugated double bonds in their molecules. Therefore, this encapsulating technology can have good potential in food and nutraceutical formulation and coatings, bioactive food packaging and processing industries.

In the second case study (5) this technique has been used to encapsulate a bioactive functional ingredient, ω-3 fatty acid. In this case, the ω-3 fatty acid encapsulated was observed to be more efficient against degradation under both ambient conditions (relative humidity and temperature) and in a confined space (so-called headspace experiment) that more closely simulates a sealed food packaging situation. By fitting the degradation data, it was seen that the encapsulated ω-3 fatty acid showed a 2.5-fold reduction in the degradation rate. In addition, headspace analysis by gas chromatography coupled with mass spectrometry showed that the presence of 3 main flavor-influencing aldehydes in the headspace was much lower in the encapsulated ω-3 fatty acid, suggesting that the encapsulated bioactive also releases much less off-flavors.

The third case study shows the application of the technique scaled-up recently by Bioinicia S.L. as a viable method for the encapsulation and stabilization of probiotics (8,9). The probiotic definition requires that the bacteria maintain its viability from production to consumption. In this context, the International Dairy Federation (IDF) has recommended that the bacteria must be alive, metabolically active and abundant in the product and also through their passage across the gastrointestinal tract to guarantee its efficacy. However, several factors influence the bacterial survival during formulation, technological processes, and storage and also controlled release in the gastrointestinal tract, including low and high temperatures, pH and relative humidity. With this purpose, we have developed and scale-up innovative technologies and equipment (Fluidnatek® brand) and made viability studies over time, under different environmental conditions (temperature and relative humidity). For all these different case studies the encapsulated probiotics survival was substantially incremented as compared to the non-encapsulated probiotic strains. These results show the potential of our proprietary electrohydrodynamic processing and equipment as a viable means for encapsulation of bacteria.

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STARCH AND THEIR DERIVATIVES AS EMULSIFIERS OF ANTIMICROBIAL CINNAMON OIL

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INTRODUCTION

Nowadays, there is a growing interest in the active food packaging materials utilizing biopolymeric coatings with various functionalities. Starch is a polysaccharide-based biopolymer that is widely used for paper coating applications and can be potentially used in conjunction with many functional additives including antimicrobial agents such as essential oils. There are various types of starches, which differ according to their chemical composition and macromolecular structure, including various content of linear amylose and branched amylopectin. Furthermore, they can be modified by physical, enzymatical or chemical altering in order to change their functional properties. One of hydrophobically modified starches is one modified with Octenyl Succinic Anhydride (OSA), and typically hydrolyzed to suitable molecular weight. For example, PURITY GUM 2000 (National Starch) is a unique emulsion stabilizing starch derived from waxy maize. Cinnamon oil has been recognized recently due to its wide spectrum of antimicrobial activity, with key bioactive ingredient cinnamonadehyde (Lopes et. al, 2011; Kapoor, 2008). It is well know, that activity of hydrophobic antimicrobial substances applied as o/w emulsion is strictly related to their size distribution of oil droplets. The objective of this study was to investigate the effect of amylose corn starch (E), amylopectin corn starch (B), and OSA starch (Purity Gum 2000) with and without addition of low molar mass o/w emulsifier Tween 20 on particle size distribution of cinnamon oil droplets.

METHODS AND RESULTS

High amylose (E) and amylopectin (B) corn starches (Cargill) were dissolved both at concentration 5% wt. in water at 95°C using mechanical stirring for 30 min. Purity Gum 2000 (National Starch) was stirred at 5% wt. in water for 24 hours with magnetic stirring. The ultrasonic processor UP400S (400 W, 24kHz) (Hielscher, Germany) was used to obtain-oil-in-water microemulsion. 0.5g of Cinnamon oil (Jiangxi global natural spice co. Itd, China) was slowly added into starch solution (50 g) and ultrasonicated for 10 min. For samples with Tween 20, firstly Tween 20 (0.5% wt.) was added into specific starch solution and ultrasonicated for 5 min, and then cinnamon oil was added and ultrasonicated again for 5 min. The partical size distribution was monitored using Mastersizer 2000 (Malvern Instruments, UK) equipped with the Hydro 2000MU wet dispersion unit. For cinnamon oil the refractive index (RI) of 1.573 was selected. Figure 1 represents the particle size distribution of cinamon oil in aq. solutions of different starches with/without Tween20.

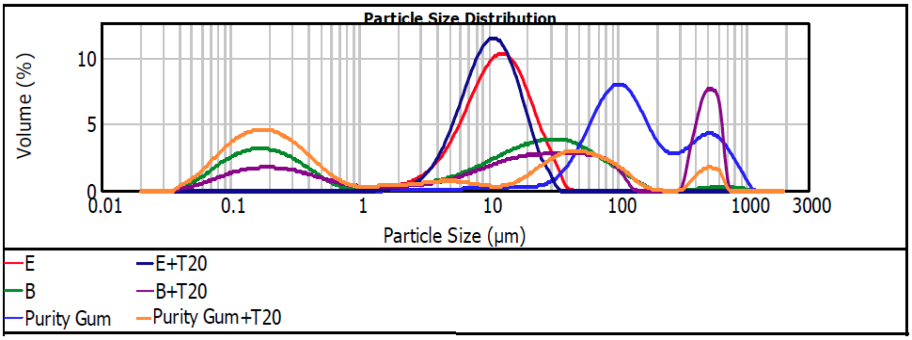

Figure 1. Cinnamon oil droplet size distribution emulsified in presence of aq. solutions of different starches (E – high amylose, B – high amylocpectin, Purity Gum – OSA starch) with and without Tween20.

CONCLUSIONS

Presence of high amylose content starch (E) lets to monomodal particle size distribution of cinnamon oil droplets with mean size in range 1-10 µm, where with addition of Tween20 there is only slight shift towards smaller droplets. For other two starches one could observe biomodal distribution, however in case of OSA starch the droplets are much larger with size in range 20-1000 µm than for high amylopectin starch (B) - in range 0,04-200 µm. Surprisingly the effect of Tween20 for both compared starches is different with formation of multimodal (3-2 peaks) distribution, where in case of OSA starch there is significant shift towards smaller droplets and for high amylopectin starch one could observe opposite changes.

Acknowledgements

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PRAWN MUSCLE PROTEINS AS SOURCE TO DEVELOP EDIBLE FILMS

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INTRODUCTION

Considerable efforts are being expended to develop new biodegradable packaging materials from natural polymers because of environmental concerns relating to synthetic plastic packaging waste. Among biopolymers extracted from biomass, proteins stand up because of the possibility of physico-chemical modification that enhances film's properties. Films from muscle soluble proteins are commonly obtained from fish; however there is no previous report on the film-forming properties of soluble muscle proteins from prawn. The objective of the present work was to explore the feasibility of the utilization of muscular proteins of prawn (*Litopenaeus vannamei*) to develop edible films studying the effect of pH, the addition of a natural cross-linker (cinnamaldehyde) and application of thermal treatment.

MATERIALS AND METHODS

Prawn protein isolate was obtained by acid solubilization and isoelectric precipitation. Film forming solutions (FFS) (2 g protein/100 mL, 25 g glycerol/100 g protein) were prepared by homogenization with an Ultraturrax blender and pH was set to 2 or 11. Each batch was divided in two parts, the one of them suffered no further treatment (pH 2 and pH 11 films) and the other one heat treated at 80 ºC/15 min (pH2_80 and pH 11_80 films). A fifth batch was also prepared, at pH 2 and added with 5 g cinnamaldehyde/100 g protein (pH 2_C film). SDS-PAGE, mechanical properties (tensile strength, σ_m; elongation at break, ε_b; Young's modulus, E), film solubility in water, opacity (Abs_{600nm}/thickness), antimicrobial activity over an inoculum prepared from a spoiled fish, and microbiological stability (total aerobic mesophilic, *Enterobacteriaceae*, lactic acid bacteria counts) of the films were determined.

RESULTS AND DISCUSSION

SDS-PAGE analysis revealed extensive protein hydrolysis at pH 11, owing to activity of proteolytic enzymes. Thermal treated FFSs showed some protein aggregation, especially at pH 11, as well as FFS treated with cinnamaldehyde at pH 2. Furthermore, the pH 11_80 FFS showed lower protein hydrolysis than pH 11 one, being attributable to enzyme inhibition. Flexible films, measuring 100 µm in thickness, were obtained from FFS. The factor that most influenced the properties of the films was the pH, films produced at pH 2 showing higher values of σ_m, ε_b and E than those at pH 11 (Table 1). Thermal treatment exerted an effect on the mechanical properties only at pH 11, owing to proteolysis inhibition and protein aggregation. Treatment with cinnamaldehyde did not cause a very evident effect on the mechanical properties, but a lower ε_b was recorded, probably due to movement constraints between protein chains due to cross-linking. Thermal treatment, pH, and cinnamaldehyde addition did exert an effect on film solubility in water (Table 1). Film produced at pH 11 was more soluble than at pH2, owing to the lower molecular weight of the protein in the polymer matrix, which is easily released to the water media. Regarding the effect of temperature, pH 11_80 film showed lower film solubility than pH 11 one, this result matches with the higher molecular weight of the protein in the latter. Protein aggregation is also the cause of the lower water solubility of pH 2_80 and pH 2_C films as compared to pH 2 film. Regarding opacity, pH 2_C film was the most transparent ($p \leq 0.05$), whereas pH 11 and pH 11_80 films were significantly ($p \leq 0.05$) more opaque than the others (Table 1). Microbiological analyses showed that films produced at pH 2 with or without cinnamaldehyde exerted antimicrobial effects over fish spoilage bacteria, and that including cinnamaldehyde was stable after 30 days of storage at 17 ºC±2 and 58% RH, as all microbial counts were under the detection limit (1 log CFU/g film) all over the storage. Prawn muscle is a feasible raw material for the production of edible films, whose physico-chemical properties may be improved thanks to the application of thermal treatment or chemical cross-linking.

Table 1. Some physico-chemical properties of films from prawn protein isolate.

Film	pH 2	pH 2_80	pH 2_C	pH 11	pH 11_80
σ_m (N)	4.36±0.68*c*	3.86±0.30*c*	4.24±0.55*c*	0.81±0.35*a*	2.58±0.46 *b*
ε_b (%)	131±15*d*	117±23*cd*	97±14*c*	14±4.9*a*	56±16*b*
E (N)	136±12*c*	120±11*c*	128±16*c*	47±13*a*	84±11*b*
Film solubility (%)	45.0±4.3*b*	29.9±5.0*a*	28.5±3.5*a*	64.4±4.9*c*	48±3.3*b*
Opacity	0.538±0.035*b*	0.488±0.062*b*	0.215±0.005*a*	2.679±0.230*d*	1.603±0.650*c*

Different letters in the same row (*a, b, c, d*) indicate significant differences among the different film samples

A NOVELL BIOBASED BARRIER MATERIALS FOR MODIFIED ATHMOSPHERE PACKAGING APPLICATIONS

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INTRODUCTION

Whey protein isolate (WPI)-based cast films are very brittle due to several chain interactions caused by a large amount of different functional groups. In order to overcome film brittleness plasticizers like glycerol (Gly) are commonly used [1]. As a result of adding plasticizers the free volume between the polymer chains increases leading to higher permeability values. The objective of this study was to investigate the effect of partially substituting Gly by hydrolysed whey protein isolate (h-WPI) in WPI-based cast films on their mechanical, optical and barrier properties. As recently published by one of the the authors it is proven, that increasing the h-WPI content in WPI-based films at constant glycerol concentrations significantly increases film flexibility while maintaining the barrier properties [2]. The present study considered these facts in order to increase the barrier performance while maintaining film flexibility.

RESULTS AND DISCUSSION

Glycerol was partially replaced by h-WPI in WPI-based cast films. The results clearly indicate that partially replacing glycerol by h-WPI reduces the oxygen permeability and the water vapour transmission rate while the mechanical properties did not change significantly. Thus film flexibility was maintained even though the plasticizer concentration was decreased [3].

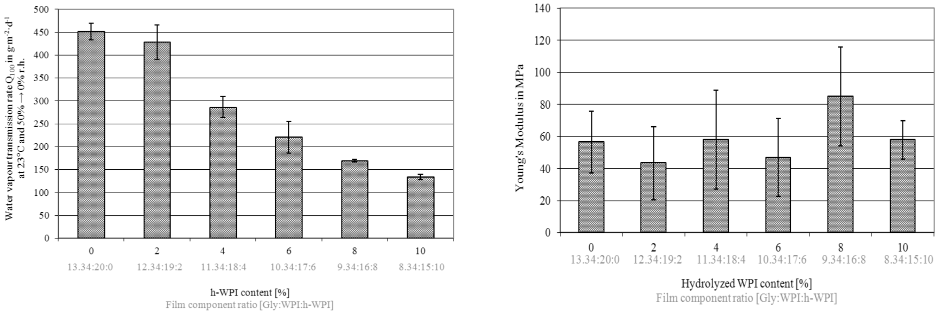

Figure 1. Effect of increased h-WPI content (reduced protein M_W) and reduced Glycerol content on the WVTR (left) and Young's Modulus (right) values of WPI-based films

CONTENTS

CONCLUSION

To the author's knowledge, this study proves for the first time the possibility of reducing the technically necessary plasticizer concentration by increasing the h-WPI concentration (M_W reduction) in formulations where the Gly concentration is reduced at the same time. This led to significantly higher barrier values while mechanical properties were maintained. This was possible since the formulations prepared in this study took benefit of the increasing flexibility when protein M_W is reduced and the decreased free volume in the protein matrixes when Gly concentration is reduced leading to decreased oxygen permeability and water vapour transmission rates.

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INITIALIZATION OF POLY(VINYL ALCOHOL) BIODEGRADATION IN SOIL ENVIRONMENT

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INTRODUCTION

PVA is used in agro-industry and agriculture as thickening and surface active agent in pesticide formulation- against insects and mites or for the production of water-soluble films containing fertilisers. However according to published studies (1,2,3), PVA is resistant to biological degradation in soil environment and could represent an environmental problem. Upon its use, PVA accumulates in the soil and can promote physic-chemical changes in its structure.

RESULTS AND DISCUSION

Biological degradation of PVA (POVAL 205, 88% hydrolisis, Kuraray, Japan) was studied in soil environment (farmland:compost - 1:5) inoculated by PVA-adapted activated sludge contaniing PVA degrading microorganisms. Biodegradability of PVA (2 g/l of soil) was followed under aerobic controlled conditions (huminidity 55%, pH_{KCl} = 6,8) employing a method for manometric determination of oxygen consumption in a respirometer (BI2000, Bioscience USA). The course of biodegradation was evaluated on the basis of determining biochemical oxygen demand, expressed as the ratio of the biological oxygen demand measured vs. theoretical oxygen demand - BOD/TOD (%). Fig. 1 shows biological degradation of PVA in soil inoculated with PVA adapted activated sludge (AAS) in comparison with soil inoculated with sterilized PVA adapted activated sludge as a control. As can be seen degradradation started almost immediately (lag-phase < 24 hours) and PVA was degraded from 54% after 30 days.

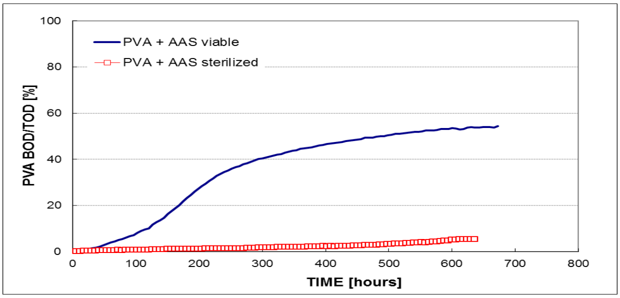

Figure 1. Degradation of PVA in soil inoculated with PVA adapted activated sludge

CONCLUSION

The experiments proved that the major drawback of PVA degradation in soil represents the absence of specific degrading microorganisms. After their addition significant biodegradation activity was detected. The long-term viability of these microorganisms in soil environment needs to be a subject of further experiments.

Acknowledgments

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PHBV/BEER SPENT GRAIN FIBRES COMPOSITES FOR FOOD PACKAGING: PROCESSABILITY AND FILM PROPERTIES

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The high cost, small processing window and poor mechanical properties of polyhydroxyalkanoates hamper their use in demanding packaging applications such as thin films. We report here on the compounding, processability and film blowing of polyhydroxybutyrate-valerate (PHBV)/beer spent grain (BSG) fibers composites. BSG are by-products from the beer industry and were submitted to an acid/caustic treatment followed by successive grinding processes to achieve BSG fibres with mean size of the order of 20 microns. BSG fibers were compounded with a commercial PHBV (ranging from 1wt% to 20 wt%) aiming at reducing the final cost of the package and improving the low melt viscosity of PHBV, thus enhancing the processability of the resulting biocomposites. PHBV/BSG fibers compounds were produced using a twin-screw mini-extruder. Processability of the compounds was studied by adding a slit die (to shape the melt into films), a cooling bath and a haul off to the mini-extrusion line (Fig 1, C, D, E, B respectively). An optimum temperature profile was found for extruding the compound, but beyond 10 wt% BSG fibers, the melt could not be further processed as rheological data indicate that a three dimensional network builds up in the PHBV matrix. However, draw down ratios as much as 25 could be achieved. The outputs of the processability study are two formulations which were scaled up for the production of thin films (from 130 to 50 microns) using a lab-scale film blowing line (Fig. 2). Electronic microscopy reveals a poor adhesion between PHBV and BSG fibers. The mechanical, structural and barrier properties of blown films (summarized in Table 1) are discussed in light of the film processing parameters studied, namely the blown up ratio and the take up ratio.

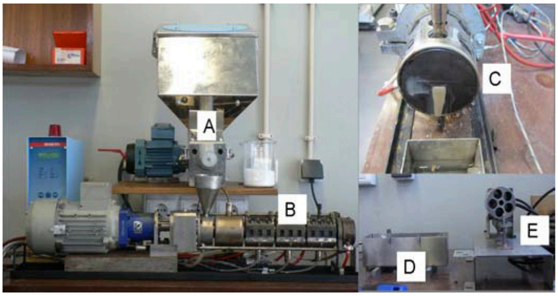

Fig 1.Flat film mini extrusion line

Fig. 2. Film blowing of PHBV

Table 1. Blow films characteristics in the machine direction

wt% BSGF	BUR	DDR	Strain at break (%)	Young modulus (GPa)	Cristallinity (Xrays - %)	O2 permeability (g*m(Pa*s*m^2)$^{-1}$)	H2O permeability (g*m(Pa*s*m^2)$^{-1}$)	Thickness (µm)
0	2-3	25	0.95-0.97	5.4-6.7	51-59	--	--	40
2	1-3	6.7-16.7	0.9-1.2	2.9-4.4	35-57	1.0-1.9 E-12	1.3-2.9 E-12	50-150
5	2-3	7.7-14.3	0.7-0.9	2.9-3.9	42-49	1.5-6.5 E-12	1.6-3.8 E-12	70-130

Acknowlegments

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GLYCOMIC TOOLS FOR THE STRUCTURAL CHARACTERIZATION OF HEMICELLULOSES: IMPACT ON THEIR EXPLOITATION FOR NOVEL-CARBOHYDRATE-BASED MATERIALS

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INTRODUCTION

Hemicelluloses from plant cell walls, mainly xylans and mannans, constitute a promising renewable resource for biofuel and biomaterial production. However, their sustainable exploitation for biofuels and biomaterials is hindered by their heterogeneous structure at the molecular level. Indeed, hemicelluloses are arguably the most structurally complex family of biomacromolecules, in terms of the stereochemistry of their constituent sugar units, the multiple possible configurations of glycosidic intramolecular linkages, and the dispersity of their macromolecular molar mass[1]. Standard methods for detailed structural determination at the levels of intramolecular linkage and macromolecular architecture are often slow and inefficient compared to routes to characterisation of nucleic acids and proteins, where routine sequencing technologies are readily available. The substitution pattern of hemicelluloses has a great influence on their physico-chemical properties (e.g. solubility, rheological and mechanical properties) but also on cell wall self-assembly by the interactions of hemicellulosic components with cellulose microfibrils and with lignins[2].

RESULTS AND DISCUSSION

In this presentation, different examples will be given on the use of plant hemicelluloses from cereals and wood for novel polymeric materials and their structural characterization at the molecular level, with special focus on the substitution pattern and the macromolecular architecture.

Mannan derivatives (cationic, anionic, and hydrophobic) have been synthesized from spruce *O*-acetyl galactoglucomannan using advanced chemical modification procedures. However, the intramolecular distribution of the modified chemical groups along the mannan backbone is not fully understood. A suitable analytical methodology has been developed combining specific enzymatic hydrolysis and advanced mass spectrometric techniques (Matrix-Assisted Laser Desorption/Ionization-MS (MALDI-MS), Electrospray Ionization-MS (ESI-MS), and Tandem MS), towards understanding the related chemical modification mechanisms. The key to the structural elucidation of the intramolecular substitution pattern of mannan derivatives of oligosaccharides is to conduct suitable MS fragmentation that is specific for one structure, providing univocal information about the sequence, branching and linkage.

On the other hand, detailed structural profiling of the side-group decorations in (glucurono)(arabino)xylans from different sources, including cereals (wheat, rye, oat) and woods (birch, beech, spruce), has been achieved using sequential and synergistic action of specific enzymes that tackle both the side groups and the backbone of the xylan chains. Furthermore, xylans from agricultural residues (wheat straw) have been employed as matrix polysaccharides combined with cellulose nanocrystals extracted from forest residues[3]. These novel all-carbohydrate composite materials exhibit enhanced thermal stability and mechanical properties, with high potential in biotechnological applications.

CONCLUSIONS

The detailed structural characterization of the substitution pattern and the macromolecular architecture of hemicelluloses require integrated glycomic approaches. Synergistic action of specific glycosyl hydrolases (GHs) combined with chromatography/mass spectrometry is required for intramolecular substitution profiling of hemicelluloses. This detailed structural characterization is fundamental for a better understanding of the modification mechanisms on hemicellulose derivatives, and for the preparation of sustainable carbohydrate-based composites with tailored supramolecular structure.

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MINIMIZATION OF RESIDUES IN THE WINERY INDUSTRY BY THE PRODUCTION OF BIOSURFACTANTS AND BIOPOLYMERS

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INTRODUCTION

Nowadays, the waste minimization is gaining attention worldwide as a renewable, widely available, cheap and environmental friendly source of carbon for biotechnological processes and for making adsorbent materials.

It has been demonstrated that vineyard pruning waste can be hydrolyzed to extract hemicellulosic sugars, which can be fermented easily and cheaply to produce valuable substances, such as biosurfactants. However, the cellulosic fraction of the lignocellulosic material remains as a by-product of this process.

In this work the cellulosic fraction of vineyard pruning waste (free of hemicellulosic sugars) was entrapped in calcium alginate beads and used to remove coloured compounds from vinasses, at the same time that hemicellulosic sugars were used as carbon source to obtain biosurfactants.

MATERIALS AND METHODS

Vineyard pruning waste was hydrolyzed in order to obtain hemicellulosic sugars that were fermented by *Lactobacillus pentosus* to obtain biosurfactants (Moldes et al., 2007). Following the cellulosic fraction of vineyard pruning waste was entrapped in calcium alginate beads using 1.25 % of vineyard pruning waste, 2.2 % of sodium alginate and 0.475 M of $CaCl_2$, in order to obtain a biopolymer, that was used as adsorbent to remove coloured compounds from vinasses. Different images of biopolymer were obtained by using a scanning electron microscope (SEM) at x33 magnification, a stereomicroscope (Nikon SMZ 1500) and a profilometer (InfiniteFocus-SL, Alicona).

RESULTS AND DISCUSSION

In this work the hemicellulosic sugars of vineyard pruning waste were used to obtain biosurfactants following the protocol used in previous works (Bustos et al., 2007), whereas de cellulosic solid fraction of this cellulosic residue was evaluated as ecofriendly adsorbent. Figure 1 shows several pictures of alginate-vineyard pruning waste biopolymer, obtained after the hydrolysis and encapsulation of vineyard pruning waste. Figure 1.a shows the macro view of the biopolymer, whereas Figure 1.b and Figure 1.c show the image of biopolymer using a SEM and stereomicroscope respectively. On the other hand, Figures 1.d, e and f show the ratio (2.07 mm), the roughness and the form of the biopolymer respectively.

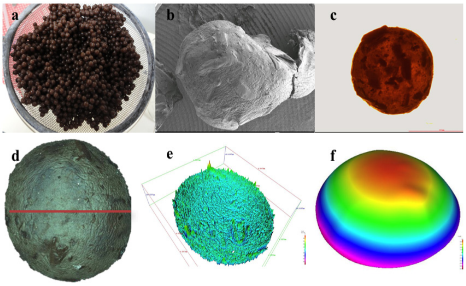

Figure 1. Pictures of the biopolymer characterization

The above biopolymer was able to remove 78 % of coloured compounds from vinasses whereas the biosurfactant obtained by the fermentation of hemicellulosic sugars from vineyard pruning waste was able to reduce in more than 16 units the surface tension of water.

CONCLUSIONS

Lignocellulose residues like vineyard pruning waste are potential renewable raw materials for obtaining biosurfactants, as well as ecofriendly biopolymers with high adsorption capacity.

Acknowledgements

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GRAPE MARC BIOPOLYMER AS NOVEL ADSORBENT TO REMOVE AMMONIA COMPOUNDS FROM FISH FARM

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INTRODUCTION

The nitrogen compounds through which toxic nitrogen is eliminated from organisms are ammonia, urea and uric acid. All of these substances are produced from protein metabolism. Ammonia is formed by the oxidation of amino groups (NH_2), which are removed from proteins when they convert into carbohydrates. It is a very toxic substance and only one nitrogen atom is removed with it. A great quantity of water is needed for the ammonia excretion. Thus, the marine organisms excrete ammonia directly in the water. The USEPA (United States Environmental Protection Agency) has established the average of the mean acute toxicity values in 2.79 mg NH_3/L for freshwater species, while the same value for seawater species has been established in 1.86 mg NH_3/L (USEPA, 1984; USEPA, 1989). In this work we propose the utilization of a grape marc biopolymer to remove ammonia from water using a biodegradable biopolymer based on grape marc entrapped in calcium alginate beads.

MATERIALS AND METHODS

Grape marc was oxidized by spontaneous biodegradation and entrapped in calcium alginate beads by mixing 2% of the grape marc with 2% of sodium alginate. This mixture was then added dropwise to a solution of calcium chloride 0.58 mol/L, in order to obtain the biopolymer. In order to carry out the adsorption process the biopolymer was added to water containing 2.72 mg/L of ammonia and 96.06 mg/L of nitrogen. The adsorption process was carried out during 2 hours at room temperature and 112 rpm; using a solid/liquid ratio of 1.5. After batch adsorption process, nitrogen was quantified by using a chemiluminescence detector, after thermo catalytic digestion, while ammonia was quantified by the colorimetric method -Berthelot's reaction-, using a segmented continuous flow analyzer.

RESULTS AND DISCUSSION

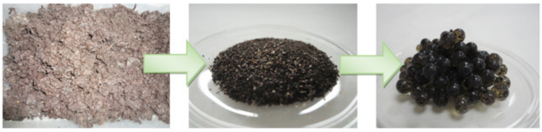

Figure 1. Formulation of grape marc biopolymer

.After the adsorption process, grape marc biopolymer was able to remove 93.8% of ammonia and 65% of nitrogen from water.

CONCLUSION

On the basis of the results obtained in this work, the biopolymer composed by grape marc entrapped in calcium alginate beads could represent a novel adsorbent to purify the water of fish farms. Thus, it could be used to improve the management and control of ammonia and nitrite levels in commercial fish farms, aquariums, ponds and fish tanks.

Acknowledgements

We are grateful to the Xunta de Galicia (project GPC, ref. CN2012/277). Vecino X. gratefully acknowledges the University of Vigo for a predoctoral contract.

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CHARACTERISATION OF INTERVERTEBRAL DISC REPLACEMENT CANDIDATE MATERIALS

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INTRODUCTION

Low back pain affects a large portion of the world's population and is a major cause of disability worldwide. In many cases low back pain has been linked to degenerative changes in the intervertebral disc (IVD). The NPmimetic project aims to develop a therapy to reconstruct and regenerate diseased IVDs by developing a minimally invasive, biologically passive scaffold to provide the necessary mechanical support, as well as an environment for cell proliferation. Due to the intended biological appication of the material, it must be sterile (often achieved via irradiation) and robust enough to withstand some period of disuse after manufacture (i.e. shelf life). The proposed scaffold would have a hydrophillic core to swell to a desired shape and size *in situ*, once implanted. We have used a combination of Fourier Transform Infrared, Attenuated Total Reflectance (FTIR-ATR) spectroscopy and Scanning Electron Microscope (SEM) to look at the effects of both γ-irradiation and accelerated ageing on the chemical, morphological and transport properties of the construct materials.

RESULTS AND DISCUSSION

Figure 1 shows the typical output from an ATR-FTIR diffusion experiment where the rate of ingress of water into the candidate material is monitored as a function of time. These experiments allow us to determine the effect that γ-irradiation and accelerated ageing have on water transport properties in such systems, as well as elucidate characteristics such as the water diffusion coefficient (D) and water-polymer interactions, which can be compared between samples subjected to different environments. In the example shown, the diffusion appears to be bimodal, perhaps pointing to a heterogeneous morphology.

Figure 2 shows typical SEM micrographs collected from the same material used to generate the data shown in Figure 1. It is quite clear that there are a number of cracks, fissures and imperfections within this material that support the findings of the diffusion experiment. Further work using thermal analysis and additional infrared spectroscopy will be conducted to enhance our understanding of this system.

CONTENTS

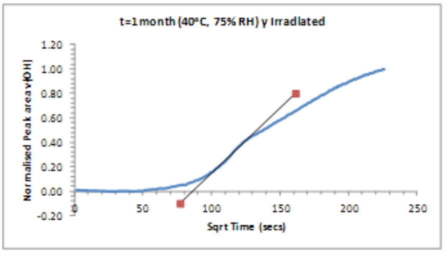

Figure 1. Plot to show the diffusion of water into a hydrophilic spinal replacement candidate obtained via FTIR-ATR spectroscopy

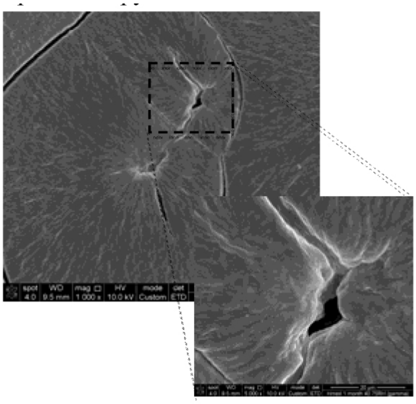

Figure 2. SEM micrograph of hydrophilic spinal replacement candidate polymer subjected to γ irradiation and an ageing process..

CONCLUSION

FTIR-ATR and SEM have been shown to be powerful techniques to elucidate important information regarding chemical changes, water diffusion properties and microscopic physical topography changes in hydrophillic, synthetic spinal replacement candidate materials as a function of γ-irradiation and accelerated ageing .

Acknowledgement

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NOVEL, PROCESSABLE POLY(N-ISOPROPYLACRYLAMIDE) NANOCOMPOSITE HYDROGELS AS STEM CELL SCAFFOLDS FOR BONE DISEASE AND NON-UNION FRACTURE THERAPY

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This presentation directly follows "Novel, Processable *Poly* (N-isopropylacrylamide) nanocomposite hydrogels as stem cell scaffolds for degenerative disc disease therapy".

Bone loss associated with degenerative disease and trauma is a significant clinical problem which is gradually worsening with an ageing population. Healthy injured bone heals spontaneously, whilst in some groups the healing/ remodelling process is insufficient, especially in cases of non-union fractures and osteoporosis. Along with organic materials such as collagen I, bone extracellular matrix in humans is about 60% hydroxyapatite. It's already used in bone substitution in orthopedics and dentistry and has been used extensively for coating implants and prosthetic joints.

Hydrogel scaffolds structurally resemble the native bone extracellular matrix and have been shown to encourage natural cell behaviours. It's also been shown that in favourable conditions, hydroxyapatite promotes MSC differentiation to osteoblasts and subsequent synthesis of new bone tissue.

We present our injectable cross- linked hydrogels as potential regenerative bone therapy materials. The system allows the facile incorporation of hydroxyapatite nanoparticles into the hydrogels prior to the addition of regenerative cells and subsequent injection.

Phase contrast inverted light microscopy was used to monitor chondrocyte (cartilage) cell behaviour during their incubation within the hydrogel matrices. In all of the presented systems, the cells have migrated, aggregated and formed a number of colonies. In the HAp- containing pNIPAM hydrogel however, the colonies appear larger and denser. All HAp-containing gel sections tested positive for calcium using Alizarin Red. The intensity of the colouring immediately surrounding the cell colonies progressively increased across each time point, which is indicative of a gradual increase in mineralisation. The findings indicate that the cells cease to exhibit cartilage cell behaviour and display characteristics of cells which have differentiated to an osteoplastic lineage.

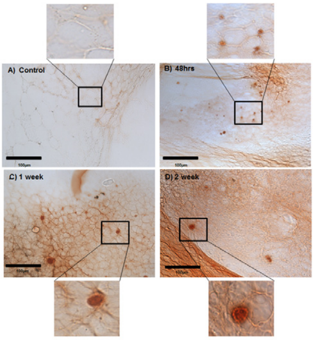

Figure 1. HAp hydrogel and control stained with Alizarin Red

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NOVEL, PROCESSABLE POLY(N-ISOPROPYLACRYLAMIDE) NANOCOMPOSITE HYDROGELS AS STEM CELL SCAFFOLDS FOR DEGENERATIVE DISC DISEASE THERAPY

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The physical and chemical characteristics of hydrogels make them attractive materials in the field of regenerative medicine, and they show enormous potential as scaffolds and stem cell delivery vehicles. The nature of a 3D cross-linked network makes post- synthetic processing and injectability extremely problematic and workers have looked at *in situ* polymerisation or stimuli responsive gelation to overcome this. This presentation highlights the invention and development of a series of novel inorganically cross-linked N-isopropylacrylamide (NIPAM) based hydrogels[1] that remain liquid indefinitely until they are cooled to a predetermined temperature, whereupon they form a hydrogel[1] that does not re-liquefy upon re-heating (Figure 1). We have successfully incorporated dopants, cast and extruded films, injected into biological tissue and electrospun these materials, elegantly demonstrating new possibilities in hydrogel processability

Figure 1. The visible process by which the polymer liquid solidifies to form a cross-linked hydrogel

Human mesenchymal stem cells (MSCs) were labelled with a green fluorescent membrane dye to enable visualisation prior to culture within or on hydrogel systems. The viability of MSCs was shown to be unaffected by the presence of the hydrogel system. MSCs adhered to the hydrogels and were shown to migrate through the system when applied to the upper surface of a solid hydrogel scaffold. MSCs were mixed with the hydrogel precursor prior to prior to solidification and maintained at 37°C for up to 4 weeks. These MSCs survived, proliferated, and synthesised matrix similar to that seen within the nucleus pulposus (NP) of human intervertebral discs (IVDs) (Figure 2). A bovine caudal disc, where the NP had been digested by collagenase treatment, was injected with the hydrogel precursor through a

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narrow bore needle. The hydrogel was shown to completely fill both the large voids formed by the collagenase treatment and also the smaller fissures caused by digestion. These initial studies demonstrate the potential for the development of a minimally invasive degenerative disc disease treatment.

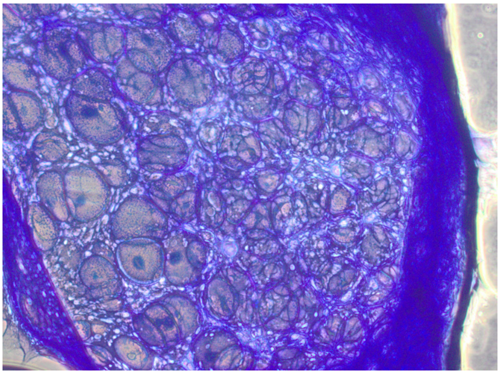

Figure 2. A histological stain at 4 weeks showing that MSCs mixed into the liquid hydrogel prior to solidification spontaneously synthesise a collagen and proteoglycan matrix similar to that seen within the nucleus pulposus of human IVDs.

References

1. Great Britain Patent GB1114446.6 Figure 1. The visible process by which the polymer liquid solidifies to form a cross-linked hydrogel.

INDUSTRIAL PROCESSES WITH POLYMERS

CONTENTS

RELEVANT PROCESS PARAMETERS FOR TWIN SCREW COMPOUNDING

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Screw conveyors have a long history. The first screw conveyor was in invented by Archimedes († 212 BC) and is still in use for irrigation. Industrial use of screw conveyors started in middle of the 19th century. Significant Industrial utilisation polymer processing began in the 1st half of the 20th century. The single extruders are used to melt and shape the polymers but they are limited in their performance. They operate with a complete filled barrel under pressure so no venting or split feeding is possible. Also their mixing capabilities are limited.

To satisfy the growing demands in the polymer industry for continuous mixing R. Erdmenger developed a co-rotating twin screw compounder with intermeshing, self wiping screws and got it patented in 1944. Various compounding tasks and the process dependent and independent parameters will be discussed in this paper. An overview how to optimize the compounding process and the screw configuration is also introduced. An automated measurement of the retention time and how to scale up the test of a small laboratory compounder to bigger pilot plant or smaller scale production extruder is presented

INJECTION OF POLYCARBONATE USING PHYSICAL FOAMING AGENTS IN A CONVENTIONAL INJECTION MACHINE

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The present work includes an experimental development in order to get foamed injected parts in Polycarbonate, with a good foaming density by means of incorporation of physical foaming agents and nucleating agents. The purpose of this development is to implement a foaming process by injection of thermoplastics adapted to a conventional injection machine, as an alternative for more expensive comercial technologies.

METODOLOGY AND PROJECT DEVELOPMENT

Figure 1 shows the steps developed in order to implement the alternative process.

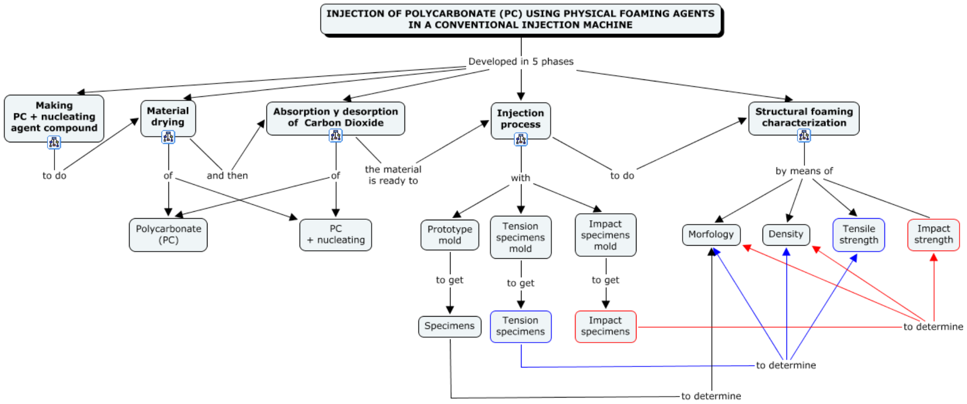

Figure 1. Steps for process implementation

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Figure 2 shows the equipments used to develope the proposed steps in the project.

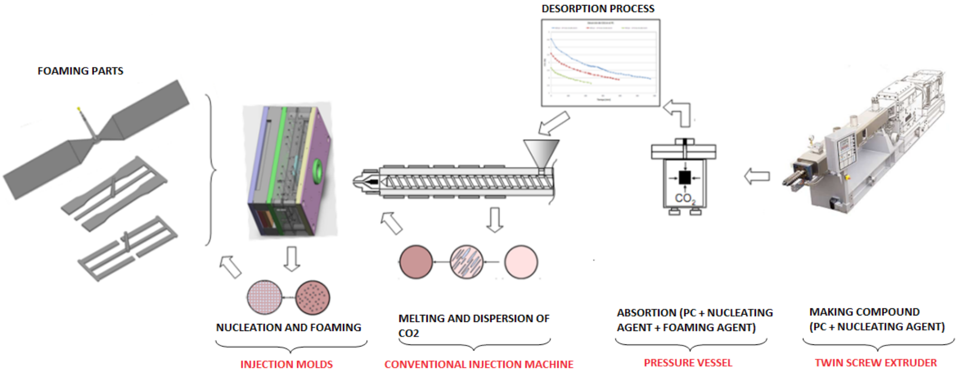

Figure 2. Equipment and experimental setup used in the process [1]

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CONTENTS

SMART TEXTILES: A STRATEGIC PERSPECTIVE OF TEXTILE INDUSTRY

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INTRODUCTION

Long time has passed, man does not take from nature what is strictly necessary any more and textile has lost the unique primary function to protect [1]. New functions are required to modern textiles: wearing comfort, durability, cleaning properties, optimized functionality for specific applications (workwear, sportswear, medical wear). Also in the case of textile industry, materials engineering and fashion designer have looked at nature as source of inspiration to create technical clothing with higher levels of functions and smartness.

RESULTS AND DISCUSSION

Smart textiles can respond via an active control mechanism for the environmental conditions called *stimuli*. Changing in their mechanical properties as well as their thermal, optical, and electromagnetic properties, in a handy manner in response to the stimuli. Application of smart textiles can be now found everywhere [2]. A lot of companies and Universities are spreading knowledge about development in smart and interactive textile material and textile processes.

An increasing number of paper (table 1 - 2) appeared in the scientific literature starting from the last two decades of last century, reflecting the growth interest of the scientific community towards smart textiles[3].

Table1. No of articles on smart textiles versus years

Years	**90 - 91**	**95 - 96**	**2000 - 01**	**2005 - 06**	**2009 - 10**
No. of Articles	26	56	87	186	247

Table 2. No. of journals and books written about smart textiles versus years

Years	**90 - 91**	**95 - 96**	**2000 - 01**	**2005 - 06**	**2009 - 10**
No. of journals and books	26 & 2	52 & 6	64 & 27	150 & 38	225 & 23

The market and the business of wearable, interactive and smart textiles are presently changing the basis of the textile industry. The Smart Fabrics and Interactive Textiles (SFIT) sector in Europe [4] is a relatively young domain and the Research, Technology and Development (RTD) activities in this area, wearable electronics and functional textiles are progressively increasing.

CONCLUSION

A new market place for smart and interactive textiles is available, in which they provide new functions and features that can enhance performance and convenience. The integration of the three giants, textiles, electronics and advanced smart materials, will produce as a result new added values to the textile industry contributing to increase the number of employers.

Acknowledgements

[1] Information on http://www.smartextiles.co.uk
[2] Information on http://www.ualberta.ca
[3] Information on http:// www.IlSole24ore.it
[4] Information on http://www.sciencedirect.com

RHEOLOGY AND FLOCCULATION IN CONCENTRATED SILICA SUSPENSIONS IN PRESENCE OF TRIBLOCK-COPOLYMER

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Interparticle attractions have a great influence on the rheology and microstructure of suspensions. In flocculated suspensions the effect of particle interaction can be investigated by measuring the rheological properties, e.g. elasticity. The used system in this research work contains oxidized and hydroxypropilated potato starch and colloidal silica particles. The silica particles carry a net negative surface charge, and have a narrow particle size distribution with a BET area of 40 m^2 /g.

In order to determine the colloidal interparticle interactions rheology experiments (e.g. rotational, oscillatory sweep and frequency sweep tests) were carried out both below and above the gelation threshold. To attain this without changing the solid content of the suspensions, thermoresponsive surfactant Pluronic F127 (PEO_n-PPO_m-PEO_n) was used. Systems that contain thermoreponsive surfactants exhibit a dramatic change in physical properties with temperature. This characteristic was used to rapidly change the suspension state from "liquid like" to "solid like" by increasing the temperature within a narrow range (Figure 1.), which allowed us to perform rheological experiments above the gelation threshold at minimum residual stresses in the dispersions.

To quantify the magnitude of interparticle interactions, we associate the liquid-gel transition with percolation theory, fractal model and elastic floc model. These models are able to detect changes in the gel network, respectively in strength of interparticle interactions with temperature increasing.

Rheological properties of wet suspensions used in industrial coating of paper are of great importance to paper coating process runnability. Rheology of paper coating suspensions is well-known to affect the structure and properties of the dry coated layers.

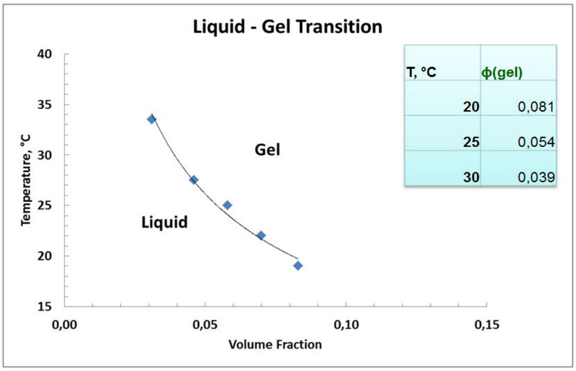

Figure 1. Liquid-gel transition diagram for mixture of 100pph silica particle, 6pph Pluronic F127 and 9pph oxydised and hydroxypropilated potato starch

Acknowledgement

The research leading to these results received funding from the European Community's Seventh Framework Programme and Marie Curie ITN under Grant Agreement No 290098-NEWGENPAK Project.

CONTENTS

VALORIZATION OF WASTES FROM AGRO-FOOD PROCESSING TO OBTAIN TRULY SUSTAINABLE BIOPLASTICS: APPLICATIONS AS SUSTAINABLE PACKAGING

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Bioplastics are generating increasing commercial interest, and indeed their market is rising at a fast pace. There are a number of drivers that are fuelling the growth in the bioplastics market, from recent technological advances are helping to bring down their cost and expand their range of properties, to the need to move away from petrochemical based materials and steer the plastics industry down a more sustainable route. However, bioplastics are still largely derived from pure feedstock such as crops and vegetable oils which may compete with food sources and diminish to some extent their true sustainability. Moreover, in terms of competing with many standard plastics, the properties of bioplastics are not sufficient for certain applications. There is undoubtedly a gap in the market for bioplastics that possess better barrier, thermo-mechanical properties and/or processability and that are obtained through a holistic sustainable approach with feedstock that do not compete with food supplies. To this end, the bioplastics industry needs to tap into new raw material sources from agro-food residues that are in abundant supply, are cost-effective, and indeed to date pose waste management and environmental challenges. In such context, biorefining, whereby microorganisms of different types can be used to convert biomass into energy or raw materials, is also an attractive alternative to conventional fossil resource refinery.

Recent research is using an integrated environmental approach to bioplastic production known as Maxi-use, whereby each stage, from sourcing to disposal, is considered in a complementary way to establish cost effective, sustainable solutions [5]. The methodology is characterised by reuse along every stage of the process, whereby a useful application for each of the compounds is investigated with a view to maximising resources to the full, thereby bringing positive impacts in terms of sustainability and profitability along the value chain. Wastes from agro-food processing can be used as raw material inputs for plastics in the packaging field, among other applications. The ability to recycle or compost the material at the end-of-life helps to redress the problem of growing and persistent volumes of land and marine waste, as well as reducing dependence on conventional fossil fuel-based resources.

Different examples of application of this approach will be given to valorise residuals from different industries and obtain sustainable materials that are highly suitable for the demands of the packaging sector. This will include the biosynthesis of polyhydroxy alkanoates (PHA) with cyanobacteria growing in olive mill waste water even without nutrients supplementation [1, 7] and the valorisation of proteins from different animal and vegetal sources into biopolymers with high barrier properties for both plastic and paper/cardboard-based packaging [2, 3, 4, 6]. Active packaging solutions using polyphenols compounds with high antioxidant effect extracted from olive waste will also be reported.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the funding from the European Community's Seventh Framework Programme [FP7/2007-2013] for the research leading to these results under the following projects:

- [1] OliPHA (grant agreement 280604): "Development of a novel and efficient method for the production of polyhydroxyalkanoate polymer-based packaging from olive oil waste water", www.olipha.eu.
- [2] WHEYLAYER (grant agreement 218340-2): "Whey protein-coated plastic films to replace expensive polymers and increase recyclability".
- [3] WHEYLAYER2 (grant agreement 315743): "Barrier biopolymers for sustainable packaging", www.wheylayer.eu.
- [4] BioBoard (grant agreement 315313): "Development of sustainable protein-based paper and paperboard coating systems to increase the recyclability of food and beverage packaging materials", www.bioboard.eu.

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COMBINATION OF DESIGN OF EXPERIMENTS, RESPONSE SURFACE METHODOLOGY AND PARTIAL LEAST SQUARES REGGRESSION ON NANOCOMPOSITE SYNTHESIS

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ABSTRACT

Synthesis and characterization of low density poly(ethylene)/organically-modified montmorillonite (LDPE/OMM) nanocomposites films was performed applying and combining three chemometric tools: design of experiments (DOE), response surface methodology (RSM) and partial least squares regression (PLSR). DOE allows the reduction of the number of experiments but maximizing the information obtained from the system. PLSR allows to find the relationships among variables and responses, how they behave in the system, and which interactions among variables are present. RSM plots are used to explore and analyze the interactions among factors and the prediction of responses on the studied experimental region.

A DOE with a central composite circumscribed design was used to perform and evaluate the influence of four processing parameters of nanocomposite synthesis: concentration of clay (Clay-%), concentration of compatibilizer (Comp-%), mixing temperature (T_{mix}) and mixing time (t_{mix}). Their influences were evaluated on six different responses: clay intercalation (d_{001}), degradation temperature ($T_{0.05}$), melting temperature (T_m), Young modulus (E), loss modulus (G'') and storage modulus (G').

A total of 27 experiments were carried out and an ANOVA-validated PLSR was used to evaluate the relationship between the processing parameters and the different measured responses using score plots, loading plots (Figure 1a), coefficient plots and RSM plots (Figure 1b). The six responses were simultaneously PLSR-modeled with a $R^2 = 0.768$ ($p < 0.05$) being Comp-% and Clay-% the most important processing parameters, and t_{mix} was the least influential parameter. Moreover, significant and complexes interactions among Comp-%, Clay-% and t_{mix} were found.

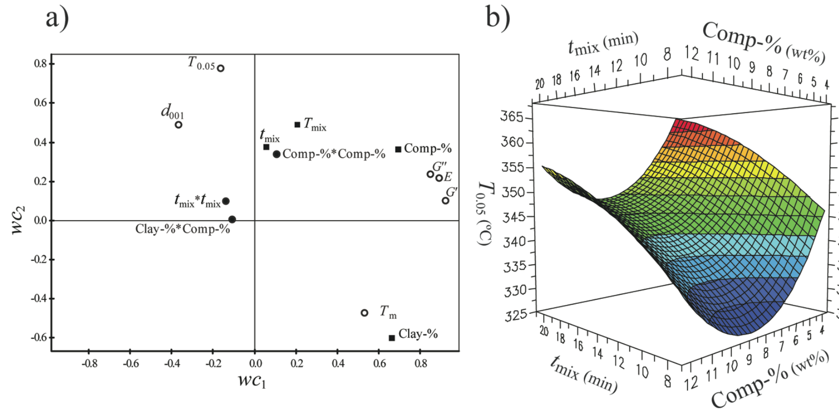

Figure 1. a) Loading plot correlating four individual variables (■), six responses (○) and three interactions among variables (●) for LDPE/OMM nanocomposite synthesis, b) response surface plot for processing parameters of LDPE/OMM nanocomposite synthesis using decomposition temperature as response ($T_{0.05}$) with fixed Clay-% = 7.0 %wt and T_{mix} = 170 ºC.

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CONTENTS

TECHNOLOGICAL PROCESS FOR COMPOUNDING WITH ALLIMENTARY ADDITIVES FOR LAYERS WITH ANTIMICROBIAL AND ANTIOXIDANT PROPERTIES

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ABSTRACT

The poster relates a obtaining process of compound polymer-based polypropylene (PP) and/or polyetilene of low density (LDPE) with additives such as chitosan activated freeze-dried 1,5-2,5%, 1076 Irganox 0,05-0,1% carnauba wax 0,01-0,02% and E vitamin 0,1- 0,5%.

Use in the manufacturing process of a special high-speed mixer with its adjustment possibilities which is facility , which allows the process of enhancement additive personally polypropylene and/or polyethylene of low density through the use of the additive type carnauba wax to certain technological parameters is a novelty in the description of classical process for compounding of polymers.

The compounds obtained on the basis of polypropylene (PP) and/or low density polyethylene (LDPE) and additives (chitosan activated freeze-dried, Irganox 1076, carnauba wax and vitamin E) confer on the product properties and multiple functionalities such as antimicrobial agent bioactive principles.

The compounds and/or films obtained were characterized by determination of induction period of oxidation and by determining the degree of inhibition of the growth of micro-organisms like *Listeria monocytogenes, Escherichia coli* and *Salmonella enteritidis,* settling material showing good antimicrobial properties and assets.

Products with special properties, antimicrobial, inhibiting a 100% increase, both gramm positive, and gram negative and all at once may be a bioactive principles by the qualities of the vitamin E so that they can be used in various branches of the food industry, pharmaceuticals and textiles

CONTENTS

COAXIAL HIGH THROUGHPUT ELECTROSPINNING ENGINEERING AND APPLICATIONS

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Due to its flexibility and versatility, electrospinning has emerged as an interesting technology to produce submicron fiber mats from natural and synthetic polymers. Co-axial and multi-axial structures, produced by concentric needles or other spinning devices, are of great interest in the encapsulation of active ingredients, enzymes, living cells, bacteria and other substances and microorganisms and also in the pharmaceutical and biomedical fields generating nanostructured biomaterials finding their application in a wide range of fields. Despite the enormous potential of this technology, it does still remain largely in a lab scale due to limited yielding from most commercial systems. Fluidnatek™ equipment and applications by Bioinicia S.L. aims at providing flexible electrospinning solutions from lab scale to pilot and industrial plants in many applications. Fluidnatek™ systems are at the state of the art of the high throughput electrospinning, providing efficient mass production solutions to scale up most of the lab developments, meeting the quality standards required by the industry.

As an example, in the field of refrigeration, the encapsulation and incorporation of phase change materials (PCMs) inside refrigeration equipment can be commercialized as a plausible solution to buffer temperature variations along the whole cold chain. To this end, structures containing PCMs can be obtained by electrospinning which are subsequently compressed to form functional structures of interest in the application.

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SPECIAL SESSION NANOCOMPOSITES FOR FOOD PACKAGING APPLICATIONS

(ACTION COST FA0904)

CONTENTS

GAS SENSING PROPERTIES OF POLYANILINE AND POLYMER/CNT THIN FILMS

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INTRODUCTION

Smart packaging systems monitor the condition of packaged foods to give information about the quality during transport and storage. Micro-sensors attached as labels, incorporated into, or printed onto a food packaging material could offer the capability to monitor the condition of packaged food or the environment surrounding the food. Polymers are a very attractive class of materials for use in sensor applications due to the fact that their chemical and physical properties may be tailored over a wide range of characteristics. In this work polymer nanocomposite and conducting polymer gas sensor devices were prepared and tested for the detection of humidity, alcohol vapor and ammonia gas.

MATERIALS AND METHODS

Two types of sensitive layers were prepared: inherited conductive polymers based on polyaniline for the detection of ammonia (NH_3) and polymer / carbon nanotubes(CNT) nanocomposites for the detection of water and ethanol vapor. Polyaniline (PANI) was synthesized directly on top of quartz substrates and then deposited in micro interdigitated electrodes using the Laser Induced Forward Transfer (LIFT) technique [1]. Conductive polymer nanocomposites were prepared by dispersing functionalized multiwalled carbon nanotubes in the polymer solution by ultrasonication. Several matrices were used (PMMA, PS, PMA, PEA, PVP, PAA). The electrical percolation threshold was studied by dc and ac techniques for PMMA/CNT films by varying CNT content [2]. The gas sensors were realized by depositing thin films of the nanocomposites on copper interdigitated electrodes of a printed circuit board by solution casting. The concentration of the target vapor in the measurement cell was adjusted by a set-up allowing controlled evaporation and mixing of the desired liquid with the purge gas (nitrogen) while ammonia concentration was controlled using mass-flow controllers. The response of the sensors to humidity, ethanol vapor and ammonia gas was examined by measuring the change in electrical resistance of the prepared active layers.

RESULTS AND DISCUSSION

It is well known that the increase of the resistance of polymer nanocomposites with conductive fillers upon exposure to volatile gases is attributed to the destruction of the conductive filler network due to polymer matrix swelling. In that sense, the connectivity of the above network is of great importance for gas sensing applications. The use of functionalized CNT leads to nanocomposites with improved filler dispersion and distribution as revealed by the morphology studies. Percolation threshold for the PMMA/CNT was estimated to be 0.21%wt. The results show a monotonically increase of response $S=(R-R_o)/R_o$ for PMMA/5%f-CNT towards ethanol vapor. Reversibility and reproducibility of the response was also observed. The nanocomposites with lower content of CNT show better response towards ethanol but considerable scattering for high relative humidities (r.h.). The instability of PMMA/CNT nanocomposites with CNT content close to percolation threshold at high r.h must be taken into account for practical sensor applications.

Furthermore, the results show that solution mixing by ultrasonication is an effective technique for dispersing carbon nanotubes in a polymer matrix with low percolation threshold. The study of the percolation threshold is important for the determination of an optimal filler concentration for gas sensing applications. CNT content should be well above percolation threshold in order to have lower signal to noise ratio. Nanocomposites with hydrophilic matrices showed higher response to water and ethanol while matrices with lower glass transition temperature showed faster response

As regards PANI sensors the response of the prepared device against time at consecutives cycles of exposure to ammonia flow at various concentrations from 500 to 2000 ppm showed the typical increase of PANI resistance when exposed to ammonia, as well as the recovery of the response after the removal of the analyte. Additional measurements indicated the good reproducibility of the response to ammonia. The above performance is adequate for the practical use of similar devices for many ammonia sensors applications.

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PROCEDURES FOR SURFACE MODIFICATION OF POLYMERS

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INTRODUCTION

In the last two decades there was a growth interest into new innovative technological developments in the production of functional foods, whose bioactive principles and actuators are either contained within packaging or as coating material.[1] Many fresh and processed foods are packaged in an inert or low oxygen atmosphere (modified atmosphere packaging - (MAP)) that can increase shelf-life four-fold, by inhibiting microbial growth and consequently food spoilage. In most circumstances, the packaging material used is polymer-based however, this has limitations. While materials such as glass and metals are impermeable to gases, in contrast plastics are semi-permeable; which can undesirably affect food and drink quality over relatively short time periods. Barrier properties of the plastics can be improved by coatings or through the inclusion of nanoparticles within the polymer matrix.

The objective of this study was to improve the quality of some polymers (poly (ethylene) and poly (lactic acid)) as food packaging materials by applying different antibacterial and antioxidant coatings.

RESULTS AND DISCUSSION

To enhance the adhesion between the polymeric substrate and the coating plasma activation was chosen. As antimicrobial agent chitosan and vanillin were used while as antioxidant vitamin E was selected. The obtained samples were analyzed by ATR-FTIR spectroscopy, XPS, potentiometric titration, scanning electron and atomic force microscopy, and goniometry. Moreover, was investigated the oxygen permeability, the antibacterial activity and the antioxidant property (by DPPH method) of the obtained materials. The properties are enhanced by applying mentioned procedures. The oxygen scavenging activity (RSA) increases with the α-tocopherol concentration (Table 1).

Table 1. DPPH radical scavenging activity of the CHT/VE-coated PE films for increasing concentrations of α-tocopherol

Sample	RSA/100 mg sample (%) (after 30 min)	RSA/100 mg sample (%) (after 24 hours)
PE	0.0	0.0
PEcor/CHT/0.5VE	25.8	77.7
PEcor/CHT/1.5VE	57.8	100.0
PEcor/CHT/3VE	83.4	100.0

CONCLUSION

The bioactive-coating of polymeric substrates led to obtaining new materials with antibacterial and antioxidant properties and with decreased oxygen permeability.

Acknowledgements

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STUDY OF THE MORPHOLOGY, THERMAL, MECHANICAL AND BARRIER PROPERTIES OF IRRADIATED POLYPROPYLENE NANOCOMPOSITES

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In the last decades, the use of polymers as food packaging materials has increased enormously due to their advantages over other traditional materials. [1] Polymer packaging provides many properties including strength and stiffness, barrier to oxygen and moisture. In order to ensure food safety, reduce post harvest losses and facilitate international trade, recently radiation technologies are always more often applied by the food industry, moreover it is a safe and environmentally clean and efficient technology.

In the field of packaging, polypropylene (PP) films hold a prominent position because of their transparency, brilliance, low specific weight, chemical inertness and good processability. Unfortunately, PP, like other polyolefins, is characterized by low barrier properties, which results in poor protection of the packaged food. [2] To overcome this drawback the incorporations a few percent of commercial nanoparticles, in particular modified montmorillonite (MMT) in a polymeric matrix, can lead to several improvements like a decrease in the package permeability to gas and aroma, and an extended shelf life for the food. [3]

The objective of this research was to study the changes of the structure and of the thermal, mechanical and barrier properties of PP/MMT films obtained by using a calandra machine, due to electron irradiation uses electrons accelerated in an electric field. The E-Beam had a fixed dose rate of approximately 10^3Gy/second.

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XANTHAN/LIGNIN MATERIALS FOR FOOD PACKAGING APPLICATIONS

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BACKGROUND

Development of food packaging applications from biopolymers has lagged behind medical materials due to high cost, low strength and poor water resistance. As an alternative, hydrogels can also offer new opportunities for design of efficient biopolymer packaging materials with desirable properties. The specialist research in technology and physical – chemical macromolecular compounds is focused in the last years on developing new materials which are finding applications in various form: films, membranes, micro – and nanoparticles, gels, etc.

Dry hydrogels from biomacromolecules exhibit a number of advantages for packaging films, particularly biodegradability and the possibility to incorporate cells, bioactive compounds and drugs. Furthermore, due to the chemical properties of functional groups along with the macromolecule backbone, hydrogels can be developed as ‘smart’ tailored devices able to respond to specific external stimuli (e.g., pH, the temperature, ionic strength and biological molecules of the surrounding medium) that act as triggers to modify over time the release rates of compounds loaded into them.

EXPERIMENTAL PART

Herein, we report the preparation of hydrogel films containing different types of lignin (HpHL-softwood sulfur free, CL-softwood Curan 100, PL-Softwood Pine, GL-lignin from annual plants, and AWL-aspen steam explosion) incorporated in xanthan gum in order to be used in food industry. These mixed xanthan/lignin hydrogels were also evaluated as matrices for vanillin release as active aroma ingredient. [1]

Xanthan gum (X) was selected for this study, due to its thickening agent, emulsifier, stabilizer qualities, and to its ability to form films, together with the possibility of applications in various areas (food industry, cosmetics and pharmacy). Lignin, presenting polyphenolic structure, has antioxidant, antimicrobial and stabilizer properties. Xanthan incorporation leads to an increase of the thermal stability, hydrophilicity, biocompatibility, biodegradability of the edible films.

The surface structure and morphology of the hydrogels were investigated by atomic force microscopy (AFM), the structural differences were evaluated by Fourier transforms infrared spectroscopy (FTIR) and the thermo-oxidative behavior was followed by differential scanning calorimetry (DSC) and thermogravimetry (TGA).

Also antimicrobial tests were done on these samples, and they evidenced the inhibition of the bacterial growth.

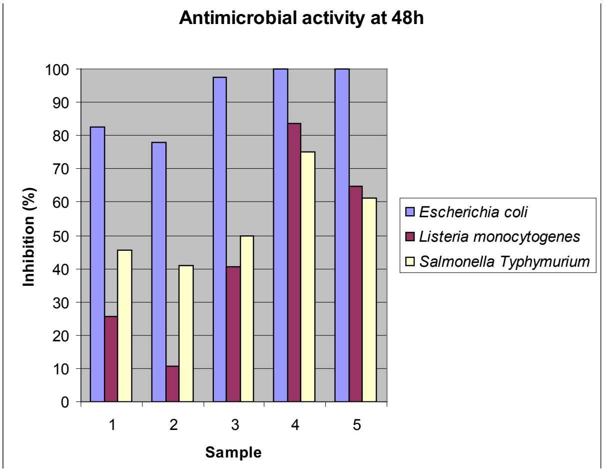

Figure 1. Bacteria growth inhibition (1 – X/HpH, 2 – X/GL, 3 – X/CL, 4 – X/AWL, 5 – X/PL)

Acknowledgement

The authors are grateful to the COST Action FA0904 for the financial support.

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POLYMERIC BACTERICIDES FROM STARCH

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INTRODUCTION

Formaldehyde, phenol, chlorine, iodine, and quaternary ammonium compounds are well known as effective antimicrobial agents [1,2]. However, low-molecular weight antimicrobial compounds exhibit numerous disadvantages, such as toxicity to the environment and humans as well as short-term antimicrobial ability. In order to overcome these problems, antimicrobial polymers – polymeric biocides can be prepared by attaching antimicrobial agents (e.g. silver, iodine) to macromolecules. Iodophors are complexes between iodine and a carrier or a solubilising agent to sustain the release of iodine and increase its solubility. Positively charged quaternary ammonium compounds can bind negatively charged triiodide anions (I_3^-) through electrostatic interaction, hence iodophors can be formed in such a way [3].

RESULTS AND DISCUSSION

During the reaction of starch with 2,3-epoxypropyl)trimethylammonium chloride, starches containing quaternary ammonium groups have been obtained. In stable iodine aqueous solutions, i.e. in the presence of iodide ions and at $pH < 7$, anionic species of iodine, first of all triiodide ($I_3^–$), could be adsorbed by quaternary ammonium groups of cationic starch according to the ion-exchange mechanism. It is well known that starch amylose forms a blue starch–iodine inclusion complex in iodine–potassium iodide aqueous solutions. Meanwhile, the colour of cationic starch (CS) iodine or CS chloride microgranules treated with aqueous potassium triiodide solution depends on the degree of substitution (DS) of modified starches (Figure 1). With increasing the DS, the colour changes from blue to yellow-brown. CS chloride with DS=0.34 forms two kinds of iodine complexes: a blue amylose–iodine inclusion complex and an ionic $CS^+I^-(I_2)_n$ complex ($n\geq1$). The content of attached iodine in the complexes depends on the DS of CS. The cationic starch–triiodide complex is more stable than the cationic starch–pentaiodide complex, however, it could release iodine into the aqueous solution of the iodine acceptor.

Thermal stability of starch iodophores decreases with the increasing content of cationic groups. The sequence of thermal decomposition temperature of complexes with iodine is *Native starch - iodine> CS – iodine (DS = 0.19)> CS - iodine (DS=0.34) > CS – iodine (DS=0.46)* which is also in accordance with the cationic groups content. The activation energy of thermal decomposition (E_a) for *CS – iodine (DS = 0.19)* is 183.4 ± 1.5 kJ/mol, and for *CS – iodine (DS = 0.46)* E_a 172 ± 5.2 kJ/mol. Such differences in thermal stability could be attributed to the different nature of complexes. Native starch forms more stable inclusion complex with iodine as compared to the ionic complexes of highly substituted cationic starches with iodine.

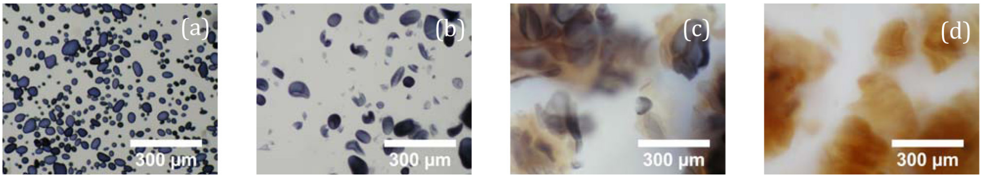

Fig. 1. Photographs of microgranules in water: a) native starch–iodine; b) CS – iodine (DS = 0.19); c) CS – iodine (DS = 0.34); d) CS – iodine (DS = 0.46)

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NEW SYSTEMS CONTAINING LIGNIN

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Much effort has been focused in recent years to develop environmentally compatible plastic products by incorporating renewable materials as an alternative to petroleum-based synthetic polymers.

Many results referring to lignin utilisation as stabilizer for plastic materials - e.g. polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), polyamide (PA), polyurethane (PU) and rubbers have been reported in literature, lignin acting also as antioxidant, modifier of mechanical properties and rigidity, its efficiency for bio-degradation capacity improvement being well known.

Poly(vinyl alcohol) (PVA) is a versatile polymer with a large amount of production annually. Blends of PVA with natural polymers such as starch, chitin, chitosan, cyclodextrin, sugar cane bagasse and other lignocellulosic fillers have been extensively studied in order to confer greater hydrophilicity and accelerated degradation while simultaneously reducing production costs. However, the intra- and inter-molecular hydrogen bonds together with the high crystallinity prevent it from melt processing. There are not so many studies on melt processing of blends containing PVA in the scientific literature, due to the fact that the melt processing of PVA is extremely difficult because of its high melting temperature, very close to the degradation temperature. That is why most of the studies on these systems have been performed in solution. For packaging or agricultural films, blow extrusion is the most frequently used technology despite a relatively high sensitivity of PVA to thermal degradation. Therefore, an increase of thermal stability of melt during processing is an essential aspect, which can positively influence the blowing technology of water-soluble PVA films.

The combination of lignocellulosic material with thermoplastic matrix in general presents a considerable problem associated to incompatibility between the polar and hygroscopic fiber and the non-polar and hydrophobic matrix.

In the present study, continuous melt mixing of some PVA/lignin systems was achieved and their physico-chemical characterization by evaluation of processing behaviour, mechanical tests, FT-IR spectroscopy and electronic microscopy is presented. A commercial maleated elastomer has been used as compatibility modifier. The particle size distribution evaluation performed in aqueous solutions by dynamic light scattering technique showed the presence of lignin nanoparticles.

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MICROCOMPOSITES BASED ON POLYPROPYLENE FOR ACTIVE FOOD PACKAGING

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Zinc oxide (ZnO) is an important electronic and photonic component for UV light-emitters, varistors, gas sensors, acoustic wave devices, etc.[1] Moreover, ZnO exhibits antibacterial activity against Gram-positive and Gram-negative bacteria.[2,] It has been reported that this activity does not require the presence of UV light (unlike TiO2), being stimulated by visible light, and it is inversely dependent on particle size.[3] Currently there was a great deal of interest in this antimicrobial property of ZnO for food packaging application, as a viable solution for stopping infectious diseases.[4]

For the aforementioned reasons and also considering their low cost, ZnO particles (of sub-micro and nano- dimensions) are ideal fillers for polymer composites. Thus, ZnO particles have been incorporated into a number of different polymers, including low density polyethylene (LDPE),[1] isotactic polypropylene (iPP),[5] polyvinyl alcohol (PVA),[6] etc., for antimicrobial purposes, for increasing dielectric and conductivity properties, mechanical and barrier properties and for reduction of polymer photo-degradation.

The aim of this work is the preparation and characterization of microcomposites based on polypropylene for application as "active packaging" in the field of "food". Zinc oxide, modified with stearic acid (ZnOm), were mixed to isotactic polypropylene (iPP) using a twin screw extruder for verifying the effect they have on the structure, morphology, thermal properties, mechanical properties, UV-visible absorption and antibacterial properties of the polymer. The ZnO particles were obtained by spray pyrolysis, the function of stearic acid is to improve the compatibility between the inorganic phase (ZnO) and the organic (iPP) one. Composites were prepared in 3 different formulations: 1,2,5% by weight of ZnOm.

Morphological analysis revealed that the extrusion process allows to obtain a good dispersion of the particles, but it also showed the presence of sporadic agglomerations, which number depends on the composition. The addition to ZnOm determines an improvement of iPP thermal stability and has a screen effect to the UV radiation. The iPP/ZnOm systems with 2 and 5% in weight of ZnOm exhibit lower stress and elongation at break values than those of iPP, but retain a ductile behavior. Finally, all systems iPP/ZnOm have significant antibacterial activity against Escherichia-coli, this activity depends on the percentage of ZnOm and on the contact time between the bacterial solution and films.

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CONTENTS

EFFECT OF NANOPACKAGING ON PRESERVATION OF READY TO EAT PASTRAMI

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Two isotactic polypropylene (iPP) based nanomaterials were tested in this study in comparison with a multilayered material (iPP/PA/EVOH/PE) for packaging of Turkish style pastrami which is made of cured and dried beef. iPP nanocomposite and active iPP nanocomposite were prepared with the addition of 1% nanoclay and with 1% nanoclay plus 5% poly-β-pinene (PβP), respectively. Sliced pastrami was packaged using these two new nanocomposites and multilayered material (control) under vacuum, modified atmosphere (50% CO_2, 50% N_2) and air (approximately 79% N_2, 21% O_2-control), and cold stored at 4°C and 50% RH for 180 days. Physical (color and texture) and chemical quality (moisture content (%), pH and lipid oxidation) and sensory properties were monitored during storage. The food relevant pathogens were not detected in the products right after the processing, on the 90th and 180th days of storage.

An important color indicator a* value representing redness for meat products was preserved better at all applications (vacuum, MAP and air atmosphere) of multilayered material with lower OTR compared to nanomaterials during whole storage. In general, a* value tended to decrease for both nanomaterial applications as the storage time increased. The decrease in the redness during storage could be related to the oxygen content in the headspace resulting in oxidation of red color pigments turning to brown. In terms of sensorial color evaluation of pastrami, all applications of multilayered material were acceptable by sensory panel during 180 days. The color of pastrami under MAP of nanomaterial and air atmosphere of active nanomaterial was acceptable for 60 days. This period was determined 120 days for vacuum applications of both nanomaterials and MAP of active-nanomaterial.

In terms of texture, maximum cutting force (N) was measured and evaluated as the hardness of the product. There was slight increase in hardness as the storage time increased for most of the applications. The hardness was 63.52 N at the beginning of the storage and ranged between 59.23-85.13 N at the end of the storage. Overall, there was no specific trend observed in terms of packaging material and the atmosphere probably due to non-homogeneous structure of the pastrami. The hardness was also evaluated by the sensory panel. Pastrami was acceptable during whole storage time at all applications of multilayer material. On the other hand, pastrami slices were acceptable for 120 days at all applications of both nanomaterials except air atmosphere of active nanomaterial which is limited to 60 days.

The initial moisture content of the product was 44.4% and did not change significantly during storage of 180 days at all applications. This could be related to low WVTR of all materials used. The initial pH of the product was 5.9 and ranged between 5.74-5.89 at the end of the storage. The limit for pH was suggested 6.0 for pastrami according to Turkish Food Codex (2012) and all pH values during whole storage were acceptable according to the law. Lipid oxidation during storage was determined as TBARS (mg MDA/kg) for pastrami. The initial TBARS was 0.27 mg MDA/kg and increased at different levels at all applications as the storage time increased. TBARS was ranged 0.39-0.47 mg MDA/kg on the 180 th day. In general, TBARS tended to be lower under vacuum for all materials tested comparing to MAP and air applications. The lowest TBARS was measured for vacuum application of multilayer material as 0.39 mg MDA/kg at the end of the storage. There was no significant difference observed between MAP and air applications of each material at the end of the storage. This could be attributed to high oxygen content at MAP and air applications of nanomaterials during storage. Although there was no initial oxygen in the headspace at MAP applications, oxygen content increased and carbon dioxide content decreased rapidly probably due to higher OTR and CO_2TR of nanomaterials compared to multilayer material. Since lipid oxidation can cause rancidity, the effect of packaging on the sensorial taste of the pastrami was also evaluated. All applications of nanomaterial and air atmosphere of active-nanomaterial were limited to 60 days in terms of taste. However, taste of the pastrami was acceptable for 90 days at MAP application of active nanomaterial and 150 days at vacuum application of active nanomaterial and at all applications of multilayer material.

Overall, the shelf life of sliced pastrami was suggested as 150 days at all atmospheres of multilayered material and at vacuum of active nanomaterial. The shelf life was limited to 90 days at high carbon dioxide application and 60 days at air atmosphere of active nanomaterial. The shelf life was also determined as 60 days for all applications of nanomaterial containing only 1% nanoclay. This study showed that active nanomaterial containing PβP could be used as an alternative to multilayer material for packaging of pastrami slices for 150 days.

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NATAMYCIN-LOADED POLY(N-ISOPROPYLACRYLAMIDE) NANOHYDROGELS FOR SMART EDIBLE PACKAGING: DEVELOPMENT AND CHARACTERIZATION

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The development of new formulations for antimicrobial agents release has attracted great attention due to the possibility of using such formulations in several applications (e.g. food packaging and surface treatments in biomedical devices). Smart packaging appears in the last years as one of the most promissory application to food packaging in order to enhance the capacity to maintain food quality and safety. Moreover, edible packaging, using edible and biodegradable biopolymers, has been stated as one of the promises in packaging science (e.g. fresh-cut products, cheese, fruits, fish). Based on this and in the fact that no work has been reported with the incorporation of smart nanohydrogels in edible packaging, a smart delivery device consisting in poly(N-isopropylacrylamide) nanohydrogels and polysaccharide-based films was developed. Polysaccharide-based films with and without the incorporation of natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels were charactherized in terms of: transport (water vapour, oxygen and carbon dioxide permeabilities) and mechanical properties (tensile strength and elongation-at-break), opacity, water sensitivity (moisture content and contact angle) and thermal properties (differential scanning calorimetry - DSC and thermogravimetric analyses - TGA). Chemical interactions were studied by means of Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy was used to verify the presence of nanohydrogel in the film matrix.

Results showed that natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels can be successfully added to edible films as confirmed by the SEM images, with the presence of nanohydrogels in film surface. The incorporation of PNIPA nanohydrogels can be done without changing the main properties of the films, however some of the physical properties of the edible films are diminished with the presence of nanohydrogels. Tensile strength values decrease ($p<0.01$) from 24.44 to 16.63 MPa, while elongation-at-break values decrease ($p<0.01$) from 15.58 to 11.91%. With the incorporation of nanohydrogels films became more opaque from 8.34 to 11.08% and showed to be more sensitive to water (i.e. higher values of moisture content and decrease of contact angle) (Table 1). From thermal analyses it can be seen that all the melting temperature values are close for all the samples, around 150 ºC, however the presence of natamycin-loaded PNIPA nanohydrogel (GA-PNIPA) lead to the increase of enthalphy of melting explained by the increase of the crystallinity of the films [1]. Thermogravimetric analyses showed similar behaviours for all samples, with the presence of four thermal events, attributed to water evaporation (from 65 to 70 ºC), chemisorbed water through hydrogen bonds (from 215 to 225 °C), dehydration, depolymerization and pyrolytic decomposition of the polysaccharide backbone (from 260 to 270 ºC) and the last thermal event related with the decomposition of the samples.

Overall, results show that the presence of natamycin-loaded PNIPA nanohydrogels led to an increase of water affinity of edible films that can be related with the capacity to bond water of the PNIPA due the presence of high numbers of hydroxyl groups at the surface of the film. In fact, the hydrophilic/hydrophobic balance of PNIPA structure is known and the hydrogen bonds formed between water molecules and hydrophilic groups possibly form a stable shell around the hydrophobic groups [2]. In conclusion, it can be stated that natamycin-loaded poly(N-isopropylacrylamide) nanohydrogels can be successfully added to polysaccharide based films and can be used as smart packaging for food applications.

Table 1. Values of moisture content, contact angle, water vapour, oxygen and carbon dioxide permeabilities (WVP, O_2P and CO_2P, respectively) of the films without (GA) and with natamycin-loaded PNIPA nanohydrogels

Film samples	**Moisture content (%)**	**Contact angle (*θ*)**	**WVP × 10^{-11} (g (m s Pa)$^{-1}$)**	**O_2P × 10^{-13} (g (m s Pa)$^{-1}$)**	**CO_2P × 10^{-13} (g (m s Pa)$^{-1}$)**
GA	17.72±0.07^{a}	112.36±6.40^{a}	5.940.82^{a}	5.84±0.87^{a}	1.970.48^{ab}
GA-PNIPA	19.16±0.27^{b}	74.48±2.09^{b}	6.480.91^{ab}	6.98±2.29^{ab}	1.820.18^{b}

Values reported are the means ± standard deviations. $^{a-b}$Different letters in the same column indicate a statistically significant difference ($p<0.01$).

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INTRODUCING MONTE CARLO TRANSPORT CODES IN PREPACKAGED FOOD IRRADIATION PROCESSES: FIRST PART

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Reports from the FAO (*Food and Agriculture Organization* of the United Nations) estimate that by 2050 food production must increase by 70% to feed the growing world population. However, improving yield is only one aspect of increasing food supply. It is equally important to conserve and protect what is already produced. Between 30 and 40% of the total produced food is lost between the stages of production and consumption. In recent years, radiation technology has shown great promise in enhancing food security, safety, and prolonging shelf-life. Moreover, irradiation treatment applyed directly on pre-packed food can prevent recontamination and facilitate prompt shipment to market. Unfortunately, food can be contaminated by radyolitic products formed in the packaging materials during irradiation. Therefore, testing packaging materials after irradiation is a fundamental part of pre-market safety assesments. This holds particularly true when novel materials or new radiation techniques are being investigated. A considerable number of experiments may be required to conducte migration studies on irradiated materials. However, irradiation experiments are expensive and time consuming. Hence, alternative approaches are desirable; computer simulations using Monte Carlo transport codes are a valid and cost-effective solution.

Monte Carlo methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical results. They are especially useful for simulating phenomena with significant uncertainty in inputs and systems with a large number of coupled degrees of freedom and they are to a wide range of fields: from computational biology to finance. In this instance, however, attention is put on their application to radiation transport. The final goal is to model and simulate the irradiation process using Monte Carlo transport codes. This modelization should be developed to account for different packaging materials, food, and types of radiation. The simulations should investigate energy deposition and absorbed dose in packaging and foodstuff. This, in return, will provide estimations of the degree of degradation and cross linking in the irradiated packaging material, of the production of radiolytic products (RPs), and of the extent of the migration of these RPs in the food. The simulations should also allow to study residual radiation and stray radiation fields present during food irradiation procedures, so to reduce as much as possible the risk for personnel and damage to the surrounding machines. Results of the simulations should be benchmarked with experimental analysis and validation.

INTRODUCING MONTE CARLO TRANSPORT CODES IN PREPACKAGED FOOD IRRADIATION PROCESSES: SECOND PART

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In recent years radiation processing technology has shown promise as one of the main techniques for enhancing food security, food safety and international trade. Food irradiation is currently allowed in over 50 countries, and the volume of food treated is estimated to exceed 500,000 metric tons annually worldwide. Furthermore, the World Health Organization stated that *"food irradiated to any dose appropriate to achieve the intended technological objective is both safe to consume and nutritionally adequate"*. However, the possibility that food is contaminated by radyolitic products formed in the packaging materials during irradiation is still present. Therefore, testing packaging materials after irradiation is a fundamental part of pre-market safety assesments. This holds particularly true when novel materials or new radiation techniques are being investigated. A considerable number of experiments may be required to conducte migration studies on irradiated materials. However, irradiation experiments are expensive and time consuming. Hence, alternative approaches are desirable; computer simulations using Monte Carlo transport codes are a valid and cost-effective solution.

Several Monte Carlo transport code are presently available. Among all, FLUKA and Geant4 are considered to be very general, adaptive, and powerful numerical methods for solving radiation transport problems, and are applied in several fields. We will here investigate the feasibility of using FLUKA and Geant4 to model and simulate the irradiation processing on prepackaged food, underlining the strength and weaknesses of both software packages. Specifically, the developed models should allow to measure the energy deposition and the absorbed dose in packaging and foodstuff as a function of different packaging materials, food, and types of radiation. This would provide estimations of the degree of degradation irradiated packaging. The simulations should also allow to study residual radiation and stray radiation fields present during food irradiation procedures, so to reduce as much as possible the risk for personnel and damage to the surrounding machines. Results of the simulations should be benchmarked with experimental analysis and validation.

CONTENTS

DETERMINATION OF ANTIMICROBIAL ACTIVITY OF PLA/SILICA BIONANOCOMPOSITES FOR FOOD PACKAGING APPLICATION

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INTRODUCTION

Polylactic acid (PLA) represent one of the most popular polyesters for various applications, and recently some of the disadvantages esspecially for food packaging application could be exceed by nanotechnology. Additon of specific nanoparticles could also, beside improvements in mechanical, thermal or barrier proprerties, have the antimicrobial effect with significant impact on shelf-life extension and food quality and safety [1,2]. Antimicrobial packaging is suitable form of active food packaging, in particular for foods where microbial contamination occurs primarily at the surface. The goal of this research was to detrmine the antimicrobial activity of PLA/silica bionanocpomosites for potential use in food packaging.

MATERIALS AND METHODS

Polymer films containing polylactic acid (PLA) as polymer matrix and different percentage (0,2%; 1% and 3%) of fumed silica nanoparticles (hydrophobic, modified with hexametyldisilazan (HMDS) with specific area of 260±30 $m^2g^{-1}$and average particle size 7 nm) were prepared. The preparation of masterbach with 10% of silica nanoparticles was conducted on twin screw exstruder. The processing paramether conditions were adjusted according to the material behavior during the extrusion. The temperature setting of the extruder from the hopper to the die was 150/170/170/170/170°C, and the screw speed was 60 rpm. Films were prepared by using a single screw extruder by casting and the temperature from the hopper to the die was 150/170/180/170/185°C, the screw speed was 50 rpm. Antimicrobial activity of prepared films was tested according to standard test method (ASTM E2149-1) for determination the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions. Antimicrobial activity of PLA films (neat and with different silica content) was tested against *Escherichia coli* (*E. coli* ATCC 8739 and *E. coli* ATCC 10536) on 20°C.

CONTENTS

RESULTS AND DISCUSSION

PLA films with 3% of silica content showed reduction in the number of initial *E. coli* (ATCC 8739 and ATCC 10536) for 63.81% and 53.87% respectively. The lowest value for reduction of test organisms showed the samples with 0.2% silica content (38.1% and 12.73% respectively) as well as 1% SiO_2 (56.19% and 38.53% respectively). The controls (PLA without SiO_2 and suspension test microorganisms without material) showed no significant change ($P < 0.05$) in the number of test organisms after 1 h incubation at 20 ° C.

CONCLUSION

Antimicrobial potential of prepared films was related to the increase of silica content in prepared samples (no reduction for neat PLA, and increase in reduction as the silica content increases). *E. coli* ATCC 8739 was more sensitive to the antimicrobial effect of the test material comapred to *E. coli* ATCC 10536. The reduction related to the increase in silica content are suggesting the antimicobial activity of silica nanoparticles which is probably due to very small particle size and great specific surface area. These results are are showing that there is a potential of PLA/silica nanocomposites as antimicrobial agent for food packaging applications.

Acknowledgements

This work was supported by the Project III 46001, Ministry of Education and Science, Republic of Serbia and COST action FA0904

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CHARACTERIZATION OF PORPHYRIN-CONTAINING POLYMERS AND THEIR APPLICATION IN ARTIFICIAL PHOTOSYNTHESIS

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Alternative sources of energy that are efficient, renewable and environmentally friendly are one of the major challenges of the world today. Photoelectrochemical (PEC) cells that use energy taken from sunlight to perform this process are a possible answer to this challenge. A PEC cell is an electrochemical device that uses sunlight energy in the absence or presence of a bias voltage to split water into H2 and O2 obtained at the cathode and anode, respectively.

Artificial photosynthesis aims to mimic the natural photosynthesis. Some of its advantages include are zero emissions, high energy density and most important, H2 can be produced from water using sunlight. Although an appreciable volume of literature has been published in this subject over the years, there is still no suitable photocatalyst which is inexpensive, stable and efficient. The goal of the research is to develop an improved photoanode for PEC cells.

The present study deals with hematite-based photocatalysts. Hematite is the mineral form of iron oxide (α-Fe2O3) and is considered very attractive as a photoanode material for water splitting application because it can absorb visible light (its band gap is about 2.2 eV), it is inexpensive, it is non-toxic and it is stable at pH>3. On the other hand, its bands alignment is not optimal when considering the potentials of protons reduction and water oxidation which means that in order to achieve efficient water splitting, we need to supply a voltage bias.

In order to increase the mass transfer efficiency and its surface area, the hematite photoanode was prepared as a foam structure. To improve the PEC process, nickel and cobalt hydroxides were added to the catalytic layer. The experimental results showed further improvement by the introduction of Oxo Tungsten Porphyrin by adsorption onto the hematite foam photoanode. The photocurrents densities obtained at 1.23 V vs. NHE for the hematite foam and the hematite foam with the nickel hydroxide and oxotungstenporphyrin additive are ~ 110 and 220 µA/ cm2.

The use of polymers in order to avoid loss of the metalloporphyrin has been attempted by hosting it in an electropolymerized layer of aniline. The Oxo Tungsten Porphyrin has been successfully incorporated into a conductive polymer matrix. Further investigation will focus on direct electropolymerization of the metalloporphyrin into the catalytic layer in order to control the amount of catalyst loaded.

CONTENTS

EVALUATION OF ANTIMICROBIAL EFFECTIVENESS OF PIMARICIN-LOADED THERMOSENSITIVE NANOHYDROGELS IN GRAPE JUICE

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INTRODUCTION

Pasteurized refrigerated (fresh) juices are the most accepted among commercial juices, however the stability of these products depends greatly on limiting recontamination by preserving the cold chain and restricting the duration of refrigerated storage after the package is opened. The use of sulphites can reduce this recontamination, however allergic disorders associated with this compound suggest that alternatives need to be used. In this work we propose the use of pimaricin-loaded poly(N-isopropylacrylamide) nanohydrogels, which can act as a protector against pimaricin degradation while allowing its controlled release.

RESULTS AND DISCUSSION

First we evaluate the antifungal effectiveness of the nanohydrogel-pimaricin system in a liquid food model system (YPD broth). We compare the effect of free pimaricin (P) and pimaricin loaded into nanohydrogels with and without acrylic acid ($NP_{PNIPA\text{-}20AA(5)}$ and $NP_{PNIPA(5)}$) with the corresponding controls without pimaricin (C, $N_{PNIPA\text{-}20AA(5)}$ and $N_{PNIPA(5)}$), in the growth of an indicator yeast (Sc 1.02). The results (Figure 1A) show that the pimaricin-loaded nanohydrogel system was highly effective at inhibiting the growth of the indicator strain. Treatments with pimaricin led to a two-fold reduction ($p < 0.05$) in the yeast growth compared to samples without pimaricin. In addition, $NP_{PNIPA\text{-}20AA(5)}$ treatment is able to extend significantly ($p < 0.05$) the latency of Sc 1.02 growth further than pimaricin alone (P), increasing from 12.39±0.54 to 81.19±0.17 h. Moreover, the advantage of using of nanohydrogels with acrylic acid can be seen when we compare the two inhibition curves ($NP_{PNIPA\text{-}20AA(5)}$ and $NP_{PNIPA(5)}$). Pimaricin-free nanohydrogels seem to have no negative effect on yeast growth.

In view of the good results obtained in the liquid food model system with the $NP_{PNIPA\text{-}20AA(5)}$ treatment, this was selected for the assay with real food (grape juice) also contaminated with an indicator yeast. The results (Figure 1B) show again that nanohydrogel does not interfere with Sc 1.02 growth, and the pimaricin treatments (P and $NP_{PNIPA\text{-}20AA(5)}$) completely inhibit the growth of Sc 1.02 through to the end of the bioassay. However, if we calculate the specific inhibition taking into acount the pimaricin concentration in the grape juice, for each treatment, we could see that the specific inhibition with the $NP_{PNIPA\text{-}20AA(5)}$ treatment is clearly higher than that of the P treatment (inset in Figure 1B).

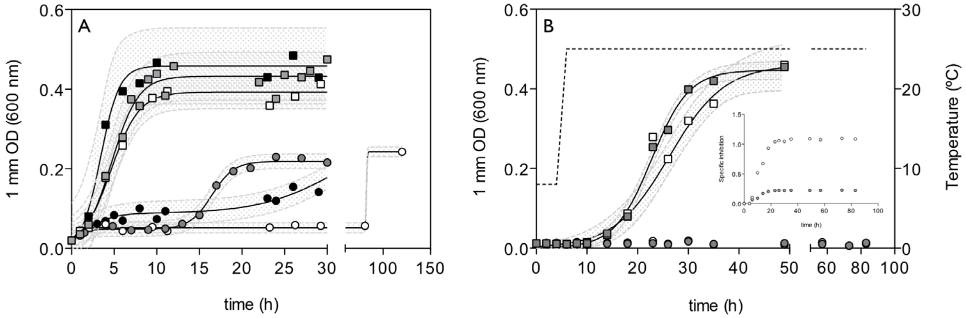

Figure 1. Effect of different antimicrobial devices on yeast (Sc 1.02) growth in a food model system (A) and grape juice (B). Control samples without pimaricin: $N_{PNIPA(5)}$ (■), $N_{PNIPA\text{-}20AA(5)}$ (□) and C (■). Samples with pimaricin: $NP_{PNIPA(5)}$ (●), $NP_{PNIPA\text{-}20AA(5)}$ (○) and P (●). The dotted area corresponds to the 95% prediction band. In B the figure inset represents the specific inhibition with time.

CONCLUSIONS

This work demonstrated the usefulness of pimaricin-loaded nanohydrogel devices to control the microbial spoilage of grape juice providing more effective inhibition which allow reduce the amount of pimaricin present in the juice. These results demonstrate the possibility of using pimaricin-loaded nanohydrogel devices in active packaging by incorporating them in food contact materials.

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STRUCTURE-PROPERTIES RELATIONSHIP IN TERNARY PP/MWCNT/OC NANOCOMPOSITES

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Among the most versatile polymers are polyolefin matrices, such as polypropylene (PP), because of their good balance between properties and cost, low density and ease in processability. Also isotactic polypropylene (iPP) is one of the most important commodity thermoplastics, accounting for about 20% of the world polyolefin production. On the other hand, carbon nanotubes (CNTs) have been considered as unique reinforcements for different polymer materials due to their exceptional physical, thermal and mechanical properties. The tensile strength, tensile modulus and Poisson ratio for CNTs have been reported to be in the range of 37–100 GPa, 640 GPa to 1–2 TPa and 0.14–0.28, respectively. Dispersion of clay nanolayers in polymer matrices usually results to exfoliated and/or intercalated polymer/clay nanocomposite, that combine the properties of ingredients and these hybrids often result to improved mechanical and thermal properties. So far, two-phase composite materials of polypropylene/clay and polypropylene/MWCNTs have been widely investigated. However, hybrid materials that combine two nanofillers particles in a polymer matrix are seldom researched. Researchers reported on extraordinary property enhancement in the case of hybrid nanocomposites incorporating two different nanophases. Only few attempts have been made to compare the mechanical properties of the conventional binary nanocomposite to a ternary nanocomposite, which combines carbon nanotubes and nanoclay as reinforcement in polypropylene matrix. Also several processing methods are available for the production of polymer/CNT composites, such as melt mixing, solution casting and in situ polymerization. Among them, melt mixing is particular desirable as it combines simplicity with speed. Among several melt mixing processes, extrusion process has captured considerable interest due to its industrial importance and its ability to disperse the CNTs in a polymer matrix.

In this study the effect of the three-phase combinations on the structure, rheological, thermal and mechanical properties of the PP/MWCNT/OC nanocomposites is investigated and compared with those of the neat polymer and the two-phase blends.

Keywords

Polypropylene, multiwall carbon nanotubes, organo-clay, ternary nanocomposites, termal properties, mechanical properties

Acknowledgments

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IMMOBILIZED POLYMER FRACTION IN POLYMER/ INORGANIC NANOCOMPOSITES

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The presented study deals with the thermal behavior of polymers and polymer nanocomposites, investigated by DSC. During isothermal crystallization of numerous polymers the base-line heat capacity decreases below the expected value when a two phase model is applied, where only rigid crystalline and mobile amorphous regions are assumed. It can be shown that the formation of a rigid amorphous fraction, which can be quantified by the heat capacity step at glass transition, satisfies the obtained value. In some polymers, the rigid amorphous fraction is developed simultaneously with the crystal formation and not upon further cooling [1]. On the other hand, it was found that polymer composites based on inorganic nano-sized fillers distributed in an amorphous polymer matrix show a rigid amorphous fraction, too [2].

In this contribution we will discuss rigid amorphous fractions in semicrystalline polymer nanocomposites. The rigid amorphous material in this class of polymers originates simultaneously from two different interaction mechanisms: (i) rigid amorphous due to interaction of the amorphous polymer with the crystals and (ii) rigid amorphous due to interaction of the polymer with the nanofillers. We present heat capacity data which allow determining fractions of different mobility for different filler contents (see figure 1).

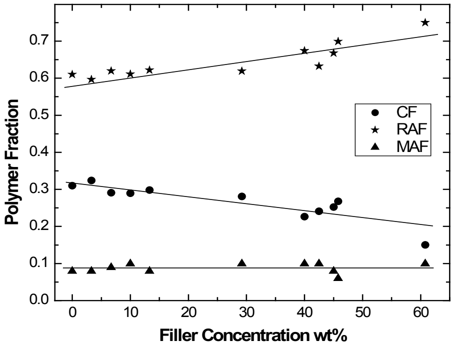

Figure 1: Rigid amorphous fraction (RAF), crystalline fraction (CF), and mobile amorphous fraction (MAF) in semicrystalline Polyamide-6.6, filled with organophilically modified layered silicate Nanofil 919 as a function of filler concentration

MAF was determined from the heat capacity step, Δc_p, at glass transition, CF from the melting enthalpy, and RAF as the remaining.

MAF+CF+RAF=1

The remaining mobile amorphous fraction in polyamide-6.6/Nanofil 919 nanocomposites seems to be independent on the filler content as well as on the total rigid fraction (RF = CF + RAF). Only the distribution of crystalline and rigid amorphous fraction changes as a function of filler content. These observation leads to the following conclusion: Crystallization can proceed as long as certain mobility is present in the amorphous fraction of the sample. In the above presented example "certain mobility" means about 10% of the sample must behave liquid like. When this limit is reached during the crystallization process, main crystallization stops and no further growth is possible, most probably because transportation of crystallizable mobile amorphous material to the growth front becomes impossible due to large amount of solid material around it.

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IONOGENIC STARCH FLOCCULANTS

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INTRODUCTION

The separation of solids from suspensions *via* flocculation is a widely used process in many fields of industry, including wastewater treatment or sludge dewatering. Mainly polyacrylamide (PAM) based flocculants are used. PAM and its derivatives, pose a number of environmental problems as some of the derivatives are non-biodegradable and the intermediate products of their degradation are hazardous to human health as their monomer is neurotoxic and carcinogenic [1]. Growing demand of environmentally friendly separation technologies promotes the interest in creation of non-toxic, biodegradable flocculants derived from natural renewable raw materials – cellulose, chitin, starch or agarose [2-4].

In this study starch derivatives containing ionogenic groups as cationic quaternary ammonium and/or anionic carboxyl groups were obtained and their flocculation properties were evaluated.

RESULTS AND DISCUSSION

Ionogenic starch derivatives containing different content of functional groups were obtained by etherification of potato starch with 2,3-epoxypropyltrimethyl ammonium chloride and modification with succinic anhydride [5]. Derivatives obtained - cationic starches (CS) with various degree of substitution (DS_{cat}=0.1-0.54) and three different amphoteric starches (AmS) containing the same amount of cationic groups (DS_{cat}=0.29) but different amount of anionic groups (DS_{an}=0.13-0.34). To confirm the structure of CS and AmS FT-IR spectra were recorded. Scanning electron microscopy was used for the evaluation of granular structure and surface morphology of modified products.

Dispersions of modified starch derivatives in distilled water were processed by mechanical shearing for 15 min at 15,000 rpm and the dispersions of fine particles were obtained [6]. Such modified starch particles have bigger surface area with better availability of functional groups and were used in flocculation experiments. Accessibility of cationic quaternary ammonium groups was detected by means of polyelectrolyte titration with dextran sulfate.

Flocculation properties of ionogenic starches were evaluated by destabilizing 0.1 wt% fine kaolin water dispersion. Residual turbidity (RT) of kaolin dispersion after destabilization was measured. It was assumed that the ionogenic starch effectively flocculates when RT is less than 10 % (named as flocculation window) and then minimal flocculant dose (mg/g of kaolin) is needed.

The obtained results showed that by increase of DS_{cat} of cationic starch derivatives from 0.1 to 0.54 the flocculation efficiency increases meanwhile the flocculation window narrows. Cationic starches with DS_{cat} 0.2 and 0.3 flocculated the best - flocculation window was from

2 to 12 mg/g. The incorporation of anionic groups into the backbone of cationic starches remarkably increased the flocculation efficiency and it depended on the amount of introduced anionic groups. Amphoteric starch with DS_{cat}=0.29 and DS_{an}=0.22 exhibited the best flocculating performance - flocculation window was from 2 to 20 mg/g. The increase of DS_{an} in amphoteric starches took a turn for the worse because a larger dose of such AmS was needed to flocculate kaolin dispersion sufficiently.

CONCLUSION

Obtained ionogenic starch derivatives - cationic and amphoteric with cationic quaternary ammonium and/or anionic carboxyl groups, have a broad flocculation window and are suitable for destabilization of kaolin dispersion. Mechanism of the flocculation was proposed and the optimal characteristics of flocculants were found.

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THE ROLE OF MULTI-COPPER ENZYMES (LACCASES) IN BIODEGRADATION OF PLASTIC MATERIAL

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Polyethylene (PE) is the most consumed plastic polymer in the world with an annual consumption rate exceeding 25 million tons per year.

Due to its high durability polyethylene accumulates in the environment at an alarming rate. The drastic accumulation of polyethylene brought attention to the need for developing microbial methods that will efficiently biodegrade plastics.

This study focused on induction and optimization of the activity of bacterial laccase enzyme produced by several polyethylene degrading bacteria. Characterization of the growth of two of the bacterial strains (designated 712 and 707) revealed that they are thermophilic (optimal growth temperature of 45°C and 40°C, respectively) and neutrophils. Further evidence showed that both strains produce extra-cellular laccase enzymes that exhibited an optimal activity at 80ºC. Several organic molecules (xylan, ABTS [2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid)] and copper) were evaluated as inducers for laccase production. Optimal treatments for laccase induction were also examined by PE biodegradation processes.

All laccase activity assays included the use of 2,6-DiMethoxyPhenol (DMP) as an indicator for laccase activity and were measured at 490nm. The induction analyses were conducted at 330nm wavelength in which maximal absorbance is received by the type III copper in laccase's catalytic site.

This study explored new ways to improve plastic biodegradation and found that biodegradation activity attributed to bacterial laccase may be enhanced in the presence of xylan and/or Cu2+. Further research is required in order to establish an efficient method for biodegradation of polyethylene.

SHAPE MEMORY STENT OF POLYLACTIC ACID COPOLYMER

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INTRODUCTION

Main purpose of this work is to report results on the shape memory effect of new biodegradable stents as well as a vaidation of the designed and manufactured prototype.

Self-expanding biodegradable polymer stent made of PLA copolymer are expected to be used in the treatment of esophageal stenosis [1]. Currently conventional metallic stents are primarily used however, they exhibit shortages as rigidity and non-degradation [2]. Therefore new promising biodegradable stents were designed and manufactured by Wroclaw University of Technology in collaboration with the Center of Polymer and Carbon Materials (PAN) in Zabrze.

The stent were prepared using highly precise laser cutting from tubes with the inner and outer diameter of 4 and 6 mm, respectively [3-4].

RESULTS

Number of test were performed to investigate the stent properties such as shape memory effects and compression strength. Numerous models have been designed, manufactured and tested in order to achieve a required shape of the stent used for further research (Fig.1).

The stents were implanted into a rabbit to evaluate *in vitro* degradation and an expected function for the treatment of *esophageal stenosis*.

It was found that the deformed stent need about 30 s to recover to its initial shape *in vitro* in 37ºC warm water and about 30 mins *in vivo* inside an animal.

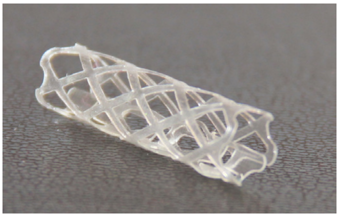

Figure 1. Photograph showing tracheal stent made of PLA copolymer.

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DEVELOPMENT AND CHARACTERIZATION OF PROTEIN NANOHYDROGELS FOR FOOD APPLICATIONS

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One of the present challenges in food engineering is the development of safe bio-systems that can protect, carry and deliver functional food components; this can be achieved using natural polymers. Protein-based nanogels have attracted considerable attention due to their non-toxicity and small dimension with a large interior network for multivalent bioconjugation, which offers several possibilities for the encapsulation of functional components by covalent attachments. Interactions between natural biopolymers, such as peptides or proteins, under specific conditions (e.g. pH, temperature, ionic strength and concentration) originate nanohydrogels that can exhibit improved functional properties in comparison to the proteins alone. The aims of the present work were to evaluate the ability of Lactoferrin and Glycomacropeptide (GMP) to form nanohydrogels. In a first stage, the electrostatic interactions between Lactoferrin-GMP were monitored by Quartz Crystal Microbalance (QCM) and a frequency decrease was observed, indicating the adsorption of Lactoferrin on GMP adsorbed surface. Subsequently, Lactoferrin and GMP nanohydrogels were produced at pH 5.8 with different concentrations (0.02, 0.1 and 0.2 % (w/v)), subjected to different temperatures vs time (60, 70 and 80 ºC for 10, 30 and 60 min) and were evaluated in terms of size distribution (hydrodynamic diameter), polydispersity and zeta potential by dynamic light scattering (DLS), turbidity measurements (UV-Vis spectroscopy at 600 nm), morphology through Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The increase in temperature and the decrease in concentration resulted in nanohydrogels with the lower values of hydrodynamic diameter (from 600 to 179 nm) and polydispersity index (from 0.499 to 0.080). This research provides important information on the effect of specific conditions (e.g. temperature, concentration, ionic strength) in the development of Lactoferrin-GMP nanohydrogels and can be useful for the design of e.g. nano-structures for food and also pharmaceutical applications.

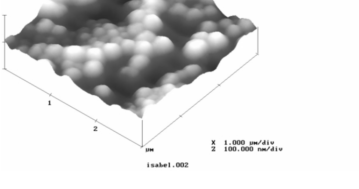

Figure 1. AFM image of the lactoferrin-GMP nanogels

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SPECIAL COST SESSION ELECTROSPINNING OF POLYMER NANOFIBERS (COST ACTION MP1206)

CONTENTS

COST ACTION MP1206 TRAINING SCHOOL ON ELECTROSPINNING OF NANOFIBRES

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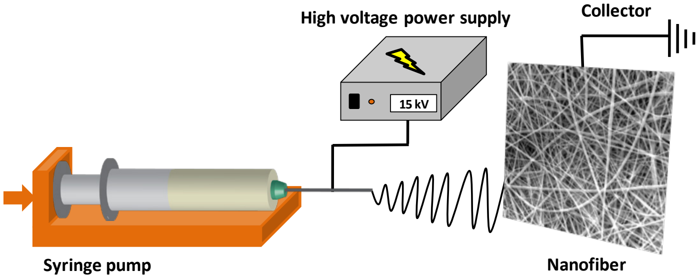
In cooperation with the Polymar conference 2013 the COST Action MP1206 is organising a training school on board of the Polymar for early stage researcher. The topic will be the production, characterization and application of electrospun nanofibres. About 30 early stage researchers have been accepted for this training school and will participate. Experienced researchers and academic teachers will perform the various high level presentations and training sessions:

- Prof. Tamer Uyar, UNAM-Institute of Materials Science & Nanotechnology, Bilkent University , Ankara, TR
- Dr Fenglei Zhou, Centre for Imaging Sciences, Institute of Population Health, The University of Manchester, UK
- Prof. Hale Karakas, Istanbul Technical University, Textile Technologies and Design Faculty, Textile Engineering Department, Istanbul, TR
- Dr. Paul D. Topham, Reader in Polymer Chemistry, Aston University, UK.
- Dr. Nabyl Khenoussi, École Nationale Supérieure d'Ingénieur Sud-Alsace, Laboratoire de Physique et Mécanique Textiles, Mulhouse, FR
- Dr. Antonella Macagnano, Institute for Microelectronics and Microsystems - National Research Scientist (CNR) Rome, IT

The COST Action MP 1206 has been started in June 2013 and will focus on electrospun nano-fibres for bio inspired composite materials and innovative industrial applications. It will continue its networking activities until May 2017.

Electrospinning, an electro-hydrodynamic process is a versatile and promising platform technology for the production of electrospun nanofibrous materials consisting of diverse polymers and polymer composites.



This platform process can provide bio- or oil based polymer nanofibrous materials for the fabrication of innovative biomedical devices and for the fabrication of new technical applications. By forming an interdisciplinary knowledge platform the COST Action MP1206 will strengthen the European R&TD on electrospun nanofibrous materials and nanofibrous composites and will generate fast progress in the state of the art. The COST Action will cover scientific breakthroughs and innovations in the electrospinning process itself, nanofibrous materials and nanofibrous composite advancements and the post treatment processing of electrospun materials. Applications in the biomedical and technical fields as well as health, societal and environmental issues are considered.

The following working groups have been started and are active in this COST Action;

- WG1 Electrospinning processes of nanofibres
- WG2 New electrospun nanofibrous materials
- WG3 Biomedical applications of electrospun nanofibrous materials
- WG4 Technical applications of electrospun nanofibrous materials
- WG5 Health/environment/societal aspects of electrospinning of nanofibres

More information can be found on the COST homepage of Action MP1206
http://www.cost.eu/domains_actions/mpns/Actions/MP1206

COST is a European Networking Activity funded via the EU R&TD program. The budget of the COST Action can be used for workshops, scientific meetings, conferences, training schools and student exchange. All interested scientists (academic and non academic) from European countries having signed up for this Action MP1206 are eligible to participate and can receive reimbursement for attending the meetings and make use of the other activities of the network (e.g. financial support for student and early stage researcher exchange). Additional participants are welcome. If interested please apply to the authors address.

CONTENTS

STABLE ELECTROSPINNING OF SILICA NANOFIBRES: INFLUENCE OF VISCOSITY

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INTRODUCTION

The sol-gel method is a well known process used to prepare materials with a variety of structures, such as powders, coatings, fibres, etc. In the sol-gel process, a three dimensional network is formed by subsequent hydrolysis and condensation reactions of an alkoxide precursor [1]. Electrospinning is an efficient technique using electrostatic forces to obtain nanofibres [2]. In combination with the sol-gel process, electrospinning showed to be suitable for the preparation of ceramic nanofibres. A detailed study on the electrospinning of silica nanofibres is essential.

METHODS

The silica sol electrospinning solutions were prepared from a mixture of TEOS, ethanol, distilled water and HCl at molar ratios of 1:2:2:0.01. First, TEOS was mixed with ethanol. Secondly, aqueous HCl solution was added to the TEOS/ethanol solution under vigorous stirring with a magnetic stir bar. Next, the solution was heated under stirring at 80°C and finally the solution was cooled down to room temperature.

RESULTS AND DISCUSSION

A key prerequisite for obtaining reproducible electrospun nanofibrous non-wovens, is the presence of a stable Taylor cone [2]. In this study sols with different viscosities were attempted to electrospin and were visually evaluated on the presence of a stable Taylor cone. Sols with varying viscosities were obtained by changing the heating time of the sols at 80°C. During the heating process, the ethanol evaporated and the TEOS started to crosslink due to hydrolysis and condensation, and thus the viscosity of the solution increased. It was found that nanofibres could be produced with sols having viscosities between 100 and 1000 mPa.s. However, stable and reproducible electrospinning resulting in uniform and beadless nanofibres was only possible in a much narrower viscosity window. The optimal viscosity window resulted in the lowest mean nanofibre diameter, having diameters in between 250 nm and 300 nm (Figure 1). Dilution of the sol may aid to easy sample prepara-

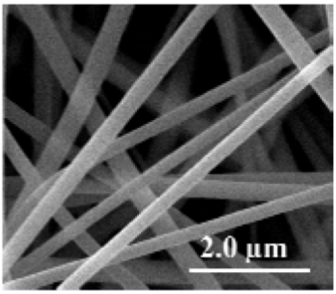

Figure 1. Reproducible silica nanofibres

tion since a specific viscosity and thus a specific fibre diameter can be easily obtained. In this study, we prepared TEOS sols with a higher viscosity than the desired viscosity. These sols were diluted with ethanol to obtain viscosities around the optimal viscosities. However, electrospinning was less stable for those diluted sols. Electrospinning with a freshly prepared sol is thus the best way to obtain uniform nanofibres in a stable, reproducible manner.

CONCLUSION

Electrospinning of TEOS sols with different viscosities was evaluated and the effect of the preparation procedure was studied. The electrospinning of freshly prepared TEOS sols was compared to the electrospinning of diluted sols, prepared from fresh sols with too high viscosities. We conclude that stable electrospinning of TEOS sols was possible in a narrow viscosity region. This region corresponded with nanofibres having the lowest mean nanofibre diameter.

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ELECTROSPINNING AND CO-ELECTROSPINNING OF BOMIMETIC NANO/MICROFIBROUS STRUCTURES

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INTRODUCTION

Electrospinning/co-electrospinning, which employs electrostatic forces to produce solid / core-shell nano/microfibres from polymer solutions, has been used to prepare biomimetic nano/microfibrous structures with potential applications in regenerating tendon/ligament and mimicking brain axons.

RESULTS AND DISCUSSION

Electrospinning coating of hybrid scaffolds

A novel approach (Fig. 1) was developed which involves coating conventional filament yarns with electrospun nanofibres [1]. The adhesion of the nanofibres to the yarn surface was enhanced by wrapping the nanofibres around the cores and a very durable coating was achieved by further plying a number of these coated cores together to create a locked multi-core yarn. The resultant microfilament core/nanofibre surface structures could mimic the hierarchical structure of tendon/ligament tissue.

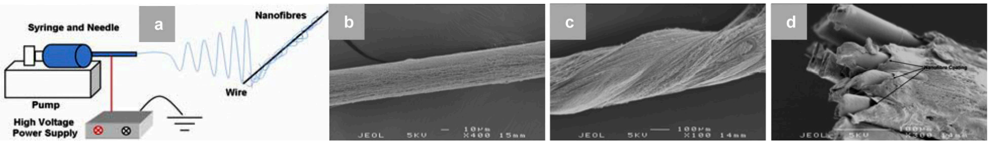

Figure 1. (a) Schematic of electrospinning coating on filament; SEM micrographs showing (b) nanofibre-coated filament; (c) longitudinal view and (d) cross-section of hybrid structure after twisting a bundle of nanofibre-coated filaments.

Co-electrospinning of hollow microfibres

We demonstrated the fabrication of polymeric hollow microfibres in a single step using the co-electrospinning of PCL and PEO solutions (Fig. 2). The resultant hollow microfibrous bundles were used to build brain axons mimicking materials for the validation of testing MRI scanners [2].

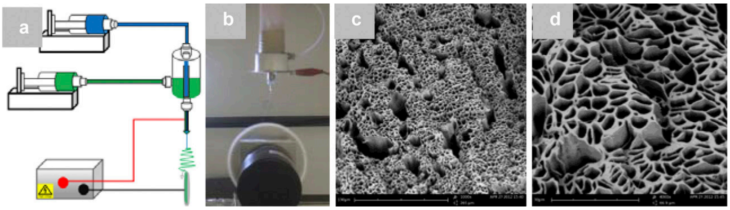

Figure 2. (a-b) Schematic and digial photo of co-electrospinning; (c-d) cross-section of co-electrospun microfibres.

CONCLUSION

Tendon/ligament mimicing fibrous scaffolds were produced by coating electrospun nanofibres on filaments, followed by twisting/plying for further nanofibre locking. Hollow polymeric microfibres were fabricated by co-electrospinning to mimic the axons in brain and further prototyped into standard MRI testing objects.

Acknowledgements

The financial support of ORS and FP7 CONNECT is acknowledged.

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CONTENTS

ELECTROSPINNING OF POLYACRYLONITRILE NANOFIBERS CHARGED BY POROUS NANO-PARTICLES

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ABSTRACT

With the outgrowth of nanotechnology, researchers become more interested in studying the unique properties of nano-scale materials. Since its discovery in 1934 by Formhals[1], electrospinning based on the formation of nanofibers by an electrostatic way has attracted more attention due to its versatility and great potential for many applications[2–7]. However, most of polymer nanofibers do not have specific functions. It is therefore necessary to add some fillers or to modify their surface. This is for example the case when an application as biosensors[8] or pressure [9,10] are targeted.

In this study, electrospinning was used for the production of composites made of polyacrylonitrile (PAN) nanofibers charged by three types of nanofillers for different potential applications. The first composite produced is composed of nanowebs of PAN charged by 4 wt. % of multiwall carbon nanotubes (MWNT) for a potential application as a pressure sensor (Fig.1-a). The second composite is constituted of nanowebs of PAN charged by 18, 20 or 30 wt. % of micron size particles of SBA-15 type ordered mesoporous silica to be used as a drug delivery system (Fig 1-b). The third composite is made of nanowebs of PAN charged by 18, 20 or 30 wt. % of montmorillonite clay particles (Na-MMT) for some applications as pollution remediation (Fig. 1-c).

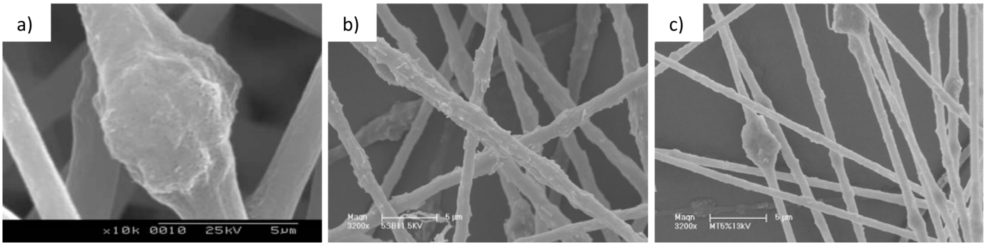

Fig. 1. Nanofibers of PAN charged by 4.5 wt. % MWNT (a), 30 wt. % SBA-15 (b) and 30 wt. % Na-MMT (c).

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CONTENTS

POLY LACTIC ACID (PLA) NANOFIBRES: PRELIMINARY STUDY OF THE EFFECT OF DIFFERENT SOLVENT SYSTEMS ON NANOFIBRE MORPHOLOGY

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INTRODUCTION

Due to the biodegradability and biocompatibility of poly lactic acid, electrospun PLA nanofibres have attracted a lot of interest in tissue engineering and biomedical applications. However, the selection of an appropriate non-hazardous solvent or solvent system is essential to determine the electrospinnability of the solution and consequently the production of nanofibres. In this study the effects of different solvent systems on PLA nanofibre morphology and mean diameter were investigated. Poly lactic acid (PLA) solutions were prepared dissolving PLA in various pure solvents and mixed-solvent systems: acetone (AC), 1,4-dioxane (DX), tetrahydrofuran (THF), dichloromethane (DCM), chloroform (CHL), dimethylformamide (DMF) and dimethylacetamide (DMAc). The most promising solvent system was then investigated in more detail. Viscosity, conductivity and surface tension of each solution were also measured, to study the effect of solution properties on the nanofibre morphology. The electrospun fibres were observed by scanning electron microscopy and image software was used to measure nanofibre diameter.

Results and discussion

Among the PLA-solutions in single solvents, only the 10% w/v PLA solution in acetone produced a sufficient quantity of PLA nanofibres to form a nanofibre mat. For the mixed solvent systems, all 10% w/v PLA solutions in mixed solvents of acetone and another solvent were spinnable and nanofibres could be collected. Larger nanofibres with a broad fibre diameter distribution were collected using the solvent systems AC/DX, AC/THF, AC/DCM and AC/CHL. Defect-free nanofibres with a narrow diameter distribution were collected using the solvent systems AC/DMF and AC/DMAc. Among the mixed solvent systems, it was found that the mean nanofibre diameter decreased as the boiling point of the second solvent in the mixed-solvent system increased as shown in Figure1. AC/DMF allowed the production of the thinnest nanofibres with a narrow diameter distribution, therefore the effect of the solvent ratio AC/DFM on the nanofibre morphology was also investigated. The results showed that increasing the amount of DMF in the solvent ratio gave thinner nanofibres with fewer defects. However the solvent ratios 40/60 and 20/80 did not produce nanofibres, probably due to either too low a value of solution viscosity or too high a value of either conductivity or surface tension, as shown in Table 1.

The results obtained suggested and confirmed that the solution properties, such as viscosity, surface tension and conductivity have a significant effect on nanofibre morphology and diameter.

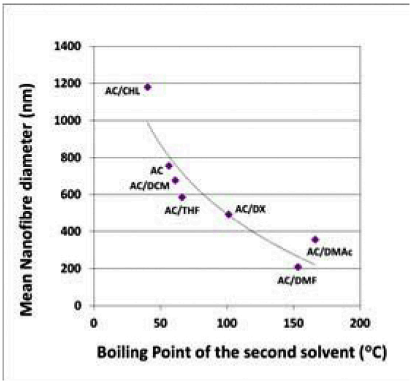

Figure 1. Boiling point of 2nd solvent vs mean nanofibre diameter

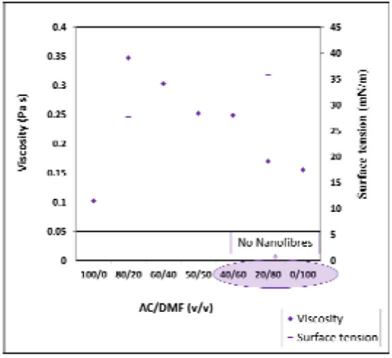

Table 1. Effect of the solvent ratio AC/DMF on mean nanofibre diameter

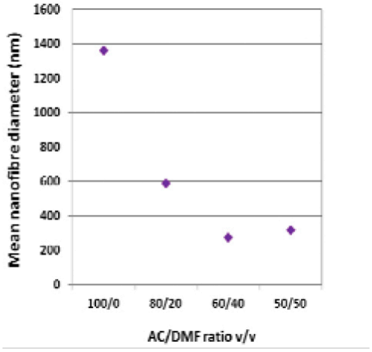

Table 2. Effect of the solvent ratio AC/DMF on solution viscosity and surface tension

FUNCTIONALISATION OF ELECTROSPUN NANOFIBRE MEMBRANES WITH TITANIUMDIOXIDE NANOPARTICLES

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Electrospun nanofibre membranes have a high water flux in comparison to other microporous structures. In this research the added value of functionalisation of nanofibers with titanium dioxide nanoparticles ($nTiO_2$) is evaluated. Titaniumdioxide nanoparticles have been used in this study because of their low cost and advanced oxidation properties. This leads to efficient removal of pathogens and recalcitrant molecules in water.

MATERIAL AND METHODS

Two possible ways of functionalisation are being studied: dip-coating and in-line functionalisation [1]. Two titaniumdioxide-solutions have been tested. Degussa P25 (Sigma Aldrich), offering a mixture of anatase and rutile TIO_2 in the range of 25 nm and a synthesized colloid consisting of faceted, single-crystalline, anatase TiO_2 nanoparticles ($nTIO_2$) with an average size of about 6 nm [2]. Photocatalytic activity of the nanofibre membranes functionalised with TiO_2 was assessed by degradation of methylene blue. The membrane was put in a methylene blue solution (10 mg/1) and illuminated by ULTRA-VITALUX lamp, 300W (Osram) for 6 h.

RESULTS AND CONCLUSIONS

Preliminary tests with nanofibre membranes functionalised with TiO2 indicated an enhanced efficiency on the removal of methylene blue with a removal of 40% (in-line functionalisation) to 60% (post-functionalisation) of the colour after 6 hours illumination with UV-A. These are promising results on lab scale.

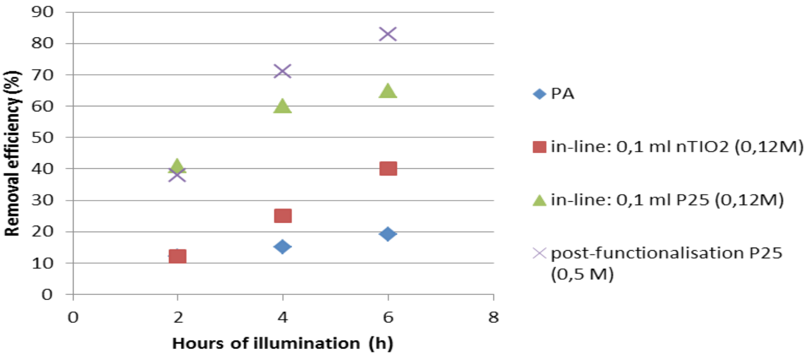

Figure 1.1: removal efficiency by different functionalised nanofibre membranes of methylene blue (intensity at 668 nm) after illumination with UVA. PA= non-functionalised polyamide nanofibre membrane. In-line: 0,1 ml TIO2 added to 20 ml spinning solution.

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INVESTIGATION OF NANOFIBRES WEB STRUCTURE UNIFORMITY MANUFACTURED BY ELECTROSPINING

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INTRODUCTION

Electrospun polymer nanofibres with diameter between 10 - 500 nm, have some unique properties, as the high specific surface area, high porosity and small diameter. Due to these characteristics nanofibres or nonwoven materials from nanofibres are often used for medical applications (bandage, artificial organs, drug delivery system), filtration, composite, protective clothing etc. [1].

It is kown, that structure of nonwoven materials from nanofibres (the diameter, shape of nanofibres, defects) is influenced by certain parameters: type, molecular weight, solution viscosity (concentration), surface tension, conductivity and temperature of polymer; technological parameters: applied voltage, the distance between electrodes, solution feed rate of polymer; electrospining ambient parameters: temperature, humidity, pressure. The influence of the same parameter on structure of nonwoven material from nanofibres is different [2].

It is important to have control over electrospinning process and to have the possibility to predict the structure of electrospun nanofibres or nonwoven material from nanofibres.

The goal of this article is to determine factors, which have influence on porous structure of nonwoven material from nanofibres manufactured by electrospinning process.

RESULTS AND DISCUSSION

In the electrospining process a web of nanofibres is formed on various surfaces, the web usually consisting of nanofibres of different diameters. The solidity and quality of porous nanofibres web was invetigated. The solution of polymer PA 6, with concentration of 18% was used for the web formation. The nanofiber webs of two different densities by Nanospider (Elmarco) were formed. During this experiment two different velosities of coating fabric moving were chosen. One velosity (0,002m/s) was for dense structure fabric moving and another velocity (0,006m/s) was for thin fabric structure moving. After fiber formation, the microscopic pictures of the web were done with SEM (Quanta FEG 200) microscope. All samples were chosen from the centre of nanofiber web. The fifty microscopic pictures for every thin and dense structure fabrics were taken. This number of pictures was chosen in oder to evaluate formed nanofibre web structure more precise and qualitative. The biggest pore was chosen in every picture and using Lucia Image 5.0 program was measured.

The biggest pores of dense structure in such measured from 467,03 till 1580,63 nm interval were get. For thin structure this interval of biggest pores of fifty samples was from 1048,15 till 4436,04 nm. It was determined, that in all microscopic pictures the biggest pore is 2,2 times bigger than average (more thin structure) and 2,03 times (more dense structure). Difference of the results is higher than usual, this shows that structure of web is very uneven. And for the structure evaluation other criterions must be chosen.

CONCLUSION

The structure evaluation results of webs from nanofibres showed that both thin and dense structures were obtained unequal. The analysis of nanofibres structures showed that data of pores evaluation by using normal distribution cannot be done.

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ELECTROSPINNING OF NANOFIBERS FROM NON-POLYMERIC SYSTEMS: CYCLODEXTRIN NANOFIBERS

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In general, electrospinning of nanofibers involves high molecular weight polymers and high solution concentrations since entanglements and overlapping between the polymer chains sustain the continuous stretching of electrified jet for uniform fiber formation, otherwise, for small molecules, electrospraying occurs which yields only beads instead of fibers. Hence, the electrospinning of nanofibers from non-polymeric systems is quite a challenge.

Cyclodextrins (CD) are cyclic oligosaccharides which are capable of self-assembly and form aggregates via intermolecular hydrogen bonding in their concentrated solutions. Such aggregates present in the CD solutions can be effective for the electrospinning of CD into nanofibers. CD are natural and nontoxic cyclic oligosaccharides having a toroid-shaped molecular structure which can form non-covalent host-guest inclusion complexes (CD-IC) with a variety of molecules including drugs, antibacterials, food additives, textile auxiliaries, etc.

In our recent studies, we have successfully achieved the electrospinning of nanofibers from CDs and CD-ICs without using a carrier polymer matrix.[1-4] Polymer-free nanofibers were electrospun from different native CD types (α-CD, β-CD and γ-CD)[1] and chemically modified CD types (HPβCD, MβCD and HPγCD)[2-3] in different solvent systems (water, DMF and DMAc). In addition, we were also able to produce polymer-free nanofibers from CD-IC of antibacterials[4] and flavors/fragrances.

We observed that the electrospinning of CDs is quite similar to polymeric systems in which the solvent type, the solution concentration/viscosity and the solution conductivity are the governing factors for obtaining uniform nanofibers. The presence of considerable CD aggregates and the very high solution viscosity were the key factors for attaining nanofibers from CDs without using polymeric carrier. The electrospinning of CD solutions containing urea yielded no fibers but only beads or splashes since urea breaks the H-bonding between the CDs and causes a prominent destruction for the self-associated CD aggregates in their solutions. The structural, thermal and mechanical characteristics of the CD nanofibers were also investigated. Although the CD derivatives are amorphous small molecules, interestingly, we observed that these electrospun CDs nanofibers/nanowebs have shown some mechanical integrity which they can be easily handled and folded as a free standing material.

CDs are already being used in filtrations pharmaceuticals, functional foods, textiles, filtrations, sustained/controlled delivery systems, therefore, having nanofiber/nanoweb may open the possibilities and extend the use of CDs in the fields of biotechnology, food, textiles, filtration or in other functional systems.

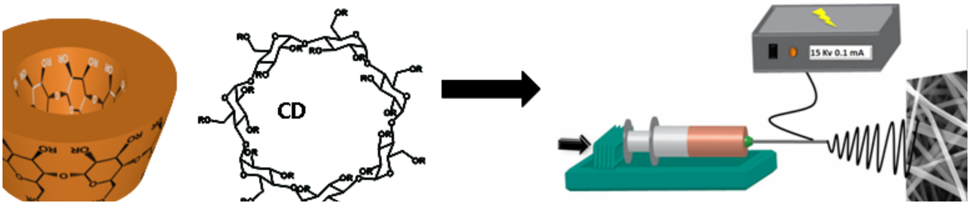

Figure 1. Schematic representations of the electrospinning of Cyclodextrin (CD) nanofibers

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GREEN AND ONE-STEP SYNTHESIS OF METAL NANOPARTICLES INCORPORATED IN ELECTROSPUN CYCLODEXTRIN BASED NANOFIBERS

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INTRODUCTION

Over the last decade, electrospinning has become the most attractive nanofiber production technique due to its versality and simplicity. Electrospun nanofibers represent unique properties like; high specific surface area, nanoscale porous structures, and distinct physical and mechanical properties[1]. In addition, these nanofibers can be easily functionalized by incorporating with metal nanoparticles (NP) which have sensing, optical, catalytic and antibacterial properties. The integration of nanofibers with NP (Au-NP and Ag-NP) enhances the applications of nanofibers in photonics, biomedicine, catalysis, sensing and nanoelectronics fields[2]. A variety of approaches were followed in the literature for the integration of nanofibers with the metal NPs. However, these methods are often complex, time-consuming, and mostly require highly toxic reducing and stabilizing chemicals, hence, simple and environmentally friendly approaches are essential for the practical applications. Cyclodextrins (CD) are naturally occurring nontoxic water-soluble cyclic oligosaccharides which are also shown to be very effective stabilizing agent for the formation of Ag-NP/Au-NP and their size control[3]. From this point of view, we adopted the use of CD molecules for Ag-NP and Au-NP incorporated nanofiber production[4].

METHODS, RESULTS AND DISCUSSION

In our studies, firstly we aimed to observe the effect of CD amounts on the Ag-NP size, so we used polyvinyl alcohol (PVA) as polymeric template and we added CD to the system at the increasing percentage. Here we did not use any additional agents for the reducing and stabilizing purposes. It was observed that the size of Ag-NP decreases significantly and homogeneous distribution of Ag-NP without aggregation were achieved in the electrospun PVA/CD nanofibers. Moreover we investigated the antibacterial property and surface enhanced Raman scattering (SERS) effect of these composite nanofibers. As the next step of our studies, we extracted the polymeric part from the system and we used CD molecules both reducing/stabilizing agent and fiber template for the fabrication of CD nanofiber composites incorporating Ag-NP via electrospinning technique. In addition to Ag-NP, we have also performed one-step synthesis of Au-NP incorporated in electrospun CD nanofibers by using the similar method. For both studies, we obtained homogenous distributions of NP through the fiber structure along with the narrow size range.

CONCLUSION

In our first approach, we carried out green and facile method for the fabrication of Ag-NP incorporated functional nanofibrous mats having SERS effect and antibacterial properties. The additional use of hazardous reducing/stabilizing agent for the formation of Ag-NP was eliminated by using CD molecules. Furthermore, polymer matrix such as PVA is also known for its biocompatible nature and suitable for biomedical applications. Therefore, these electrospun PVA/CD/Ag-NP nanofibrous mats can be quite applicable as a wound healing material, in sensing or other biomedical uses. In the second approach, we achieved the one-step synthesis of Ag-NP and Au-NP incorporated in electrospun CD nanofibers without using a carrier polymeric matrix. Therefore, the very high surface area of nanofibers is combined with the unique functionality of NP and CD molecules. These composite nanowebs would find a wide range of biomedical applications due to their biologically compatible characteristics as well as the specific inclusion complexation ability of the CD molecules.

Acknowledgements

State Planning Organization (DPT) of Turkey is acknowledged for the support of UNAM-Institute of Materials Science & Nanotechnology. Dr T. Uyar acknowledges EU FP7-Marie Curie-IRG for funding NANOWEB (PIRG06-GA-2009- 56428). A. Celebioglu acknowledges TUBITAK-BIDEB for National PhD Scholarship.

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CONTENTS

ELECTROSPUN NANOFIBERS INCORPORATING CYCLODEXTRIN INCLUSION COMPLEXES OF BIOACTIVE COMPOUNDS FOR FOOD PACKAGING

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In the recent years, incorporation of bioactive compounds with antibacterial and/or antioxidant properties have been studied for designing active food packaging materials to prevent foodborne diseases, provide safety/quality of nutrition and extend shelf life of food.[1] Very recently, electrospun nanofibers have received some consideration as an active food packaging material due to their very large surface area to volume ratio, nanoscale porosity and high encapsulation efficiency of active compounds.[2] However, these active compounds having volatile nature may encounter problems related to quick release during the electrospinning process or during the storage of the nanofibers.[3]

Cyclodextrins (CD) are non-toxic cyclic oligosaccharides having truncated cone shaped molecular structure, the CD cavity has the ability to form non-covalent inclusion complexes with many different types of guest molecules.[3] Volatile and/or unstable food additives such as flavors, antioxidants, essential oils can be protected from evaporation, degradation and oxidation by forming CD inclusion complexes (CD-IC).[4,5] Controlled/slow release, prolonged shelf-life and high temperature stability for these food additives and bioactive compounds could be achieved by CD-IC.[4,5]

The incorporation of CD-IC into electrospun nanofibers is quite interesting, since these functional nanofibers have not only high surface area and nanoporous structure, but also the specific properties of CD-IC.[3,6] Volatile active compounds having high thermal stability, slow release and prolonged shelf-life could be achieved by encapsulation of their CD-IC into electrospun nanofibers. [3,6]

In our studies, electrospun polyvinyl alcohol (PVA) nanofibers encapsulating CD-IC of bioactive compounds such as vanillin, geraniol and eugenol were obtained via electrospinning.[3] These compounds are widely used as fragrance and flavor and it is also used as a food preservative due to their antioxidant and/or antibacterial properties in food industry. However, they have low stability because of their volatile nature, and they are easily oxidized or decomposed in the presence of oxygen, light or heat. We have observed enhanced thermal stability and slow release of these compounds by CD-IC encapsulated in electrospun polymeric nanofibers.[3] In another study, the CD-IC of triclosan, a practically water-insoluble antibacterial agent, were incorporated in polylactic acid (PLA) nanofibers via electrospinning.[6] The resulting nanofibers have shown better antibacterial properties against Staphylococcus aureus and Escherichia coli compared to the system of without CD-IC possibly due to the enhanced solubility and effective release of triclosan into agar medium by CD-IC.[6] Polyvinyl alcohol (PVA) or polylactic acid (PLA) were selected as a polymeric matrix, since they are proper polymer type for food packaging. As a result, these multifunctional electrospun nanofibers incorporating CD-IC of bioactive compounds are quite applicable in food packaging.

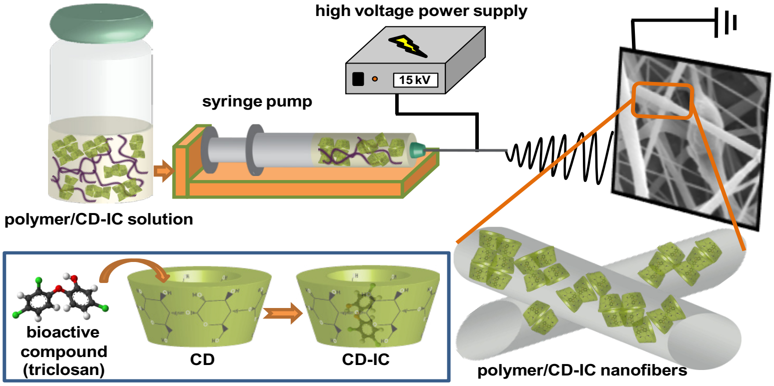

Figure 1. Schematic representations of the formation of CD-IC and electrospinning of polymer/CD-IC solution

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EVALUATION OF QUALITY OF WEB FROM ELECTROSPUN NANOFIBRES

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INTRODUCTION

The web of electrospun nanofibres usually consists of different diameter nanofibres. The diameter can vary from less than 100 nm to 1500 nm. There are a lot of parameters that affect the electrospinning process and the morphology of nanofibres. The average value of diameter is very important for nanofibre characterization, but to compare the average values is uncomplicated when dispersions of diameters are uniform. However, the analysis of various works showed that distributions of nanofibre diameter always differ; it means that only the average diameter can not be used for nanofibre characterization. For this reason the new method for nonwoven structure estimation is needed.

RESULTS AND DISCUSSION

The web of nanofibres was formed by electrospinning equipment "Nanospider^{TM}" (Elmarco, Chech Republic). Distributions of nanofibres diameter, when the speed of support material was changed are presented in Figure 1.

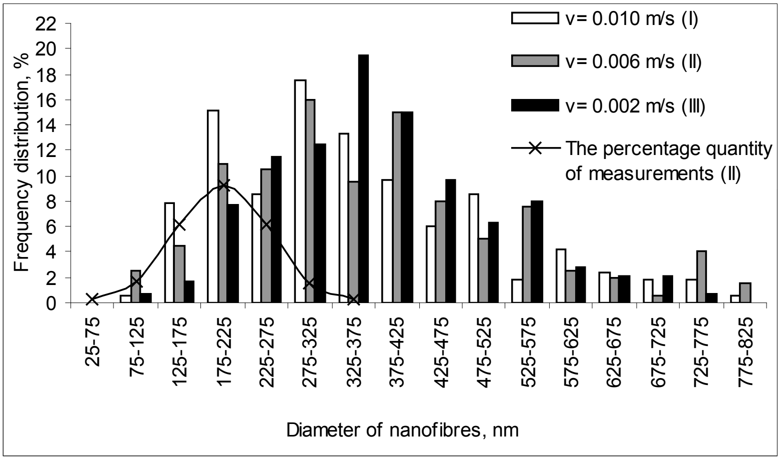

Figure 1. Frequency distributions of nanofibres

It is obvious that diameter in all cases is distributed in different distributions. With the average diameter of nanofibres, the modal value and the percentage quantity of measurements of the first distribution are proposed to use for estimation of web structure. The average diameter of the I, II, and of the III part of experiment is $\overline{d}$ = 357 nm, $\overline{d}$ = 373 nm and $\overline{d}$ = 382 nm, respectively. The difference between values is less than ± 3.5 %. The percentage quantity of values distributed in the first distribution is 32.2 % (I); 24.04 % (II see Fig.1) and 87.87 % (III). The modal value of the I also of the II variant is 200 nm, while the modal value of the III variant is 350 nm. The average of the first modal value and of the second highest peak can be used for the structure of web estimation too. From the histograms (Fig.1) the average diameter of two peaks has been calculated: d' = 250 nm (I), d' = 350 nm (II), d' = 350 nm (III).

CONCLUSION

It is not correct to compare average values when dispersions of diameter are different. The modal value, the percentage quantity of measurements of the first distribution and the average diameter of two peaks can be used with the average diameter of nanofibres for estimation of nonwoven structure. According to these criterions, it is evident that the speed of support material does not have a significant influence on the average value of nanofibres diameter but have a significant influence on the structure of web.

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CONTENTS

THE EFFECT OF ELECTROSPINNING PARAMETERS ON PCL ELECTROSPUN NANOFIBER MATS

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ABSTRACT

In this paper, the effect of electrospinning parameters (solution concentration, applied voltage, solvent composition and distance from tip-to-collector) on polycaprolactone (PCL) nanofiber mats are assessed. The diameter of the fibers are strongly related to the changes in these parameters. PCL pellets are dissolved in the mixture of tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) and electrospinning technique is applied for obtaining nanofibers. While experiencing electrospinning, the variables, namely applied voltage, tip-to-collector distance and solution concentration are changed and nanofiber mats with diameters ranging from about 100 nm to 1µm are achieved. *Key Words– polycaprolactone (PCL), electrospinning, nanofibers, process parameters.*

INTRODUCTION

Electrospinning is an advantageous method for producing nanofibers by using high voltage supplier, a charged polymer jet, needle and a collector. The polymer jet is ejected towards the collector via high electrical field [1,2].

MATERIALS AND METHOD

In this study, polycaprolactone, which is a hydrophobic, biodegradable and biocompatible polymer used especially in tissue engineering applications [3,4], is dissolved in THF /DMF solution with volume ratio 50/50 and 80/20. PCL was purchased from Sigma Aldrich and the average moleculer weigth of it is 50,000.Electrospinning is applied by using voltage between 10-15 kV,the distance from tip-to-collector is chosen as 10 and 15 cm with respect to 20 wt % and 25 wt % PCL concentration.The flow rate is kept constant at 1 mL/h and the experiment is performed under room temperature.

RESULTS AND DISCUSSION

The resultant nanofibers are observed to have a diameter ranging between 100 nm and 1µm. It has been observed that increasing applied voltage and solution concentration lead to the decrease of the diameter of nanofibers [5,6].

Considering the SEM images it can be concluded that the most homogeneous nanofibers have been obtained with the parameters as 20 wt % concentration, 80/20 THF /DMF volume ratio, 10 kV applied voltage and 15 cm distance between the needle tip and target.

CONCLUSION

The average diameter is approximately measured as 400 nm, which is reported in the literature as suitable fiber diameter to be used in artificial scaffolds [7]. The obtained nanofibers can be regarded as candidate materials to be used in tissue engineering as an artificial scaffold.

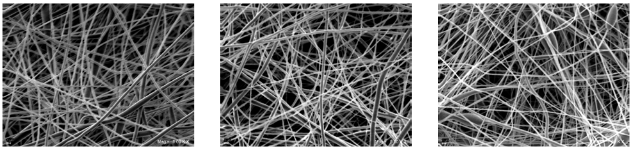

Figure 1. SEM images of nanofibers

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THE EFFECT OF ELECTROSPUN POLYAMIDE 6 NANOFIBRES ON THE MECHANICAL PROPERTIES OF A GLASS FIBRE/EPOXY COMPOSITE

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INTRODUCTION

Owing to their light weight and high stiffness and strength, fibre reinforced epoxy resin composites are widely used in industry. However, an epoxy matrix is a brittle material, which could lead to unexpected failure of the composite. Thus, an improvement of the resin rich region between two plies with a different fibre orientation is recommended [1]. Therefore, secondary (sub)micron reinforcements are often incorporated in the matrix. Nanoparticles such as carbon nanotubes (CNT) and nanoclays can be added to the epoxy matrix to improve the mechanical properties of the matrix [2]. Due to their theoretical high stiffness and strength, CNT might improve the matrix characteristics. However, the overall improvement in mechanical properties such as stiffness and fracture toughness of the epoxy matrix is mostly very moderate [2]. The main disadvantage with these CNT's and nanoclays, besides the safety issues due to the small dimensions, is the difficulty to obtain a homogeneous dispersion of the nanoparticles in the resin [2]. Moreover, the viscosity of the resin increases significantly when nanoparticles are added. The toughness of a matrix can also be improved by incorporation of rubber particles or embedding thermoplastic inclusions [3]. But again, a homogeneous dispersion of the particles in the matrix is hard to obtain. Thermoplastic nanofibrous structures offer a solution for the dispersion issue, since they can be readily embedded in the resin and a nanosized phase is incorporated in the composite. Moreover, these nanofibres don't increase the viscosity of the resin and no health hazards are involved in the production and use of these nanofibres, due to their macro scale length. Recent literature indicates that nanofibres contribute substantially to the ductility and fracture toughness of the composites [4]. This is related to the hypothesis that a secondary fibrous structure with a pronounced lower fibre diameter, in addition to a primary fibre structure, may increase several mechanical properties of composite materials.

RESULTS AND DISCUSSION

Incorporation of nanofibres increases the stress at failure in the 0°-direction. The best results are obtained when nanofibres are directly electrospun on the glass fibres. Optical microscopic images also demonstrate that nanofibres prevent delamination when a 90°-crack reaches a neighbourly 0°-ply (Fig 1). The tensile experiments under 45° demonstrate that the deposited nanofibres facilitate the load transfer to the glass fibres thereby increasing the shear stress (Fig 2). Generally, it can be concluded that the addition of polyamide 6 nanofibres improves some mechanical characteristics of a glass fibre/epoxy composite.

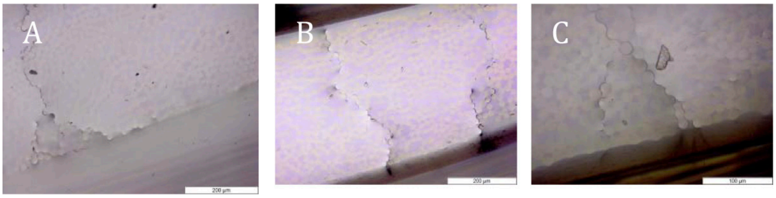

Figura1: Optical microscopy images of the failed composites: glass fibre composite (A), deposited nanofibres (B), interlayered nanofibres (C)

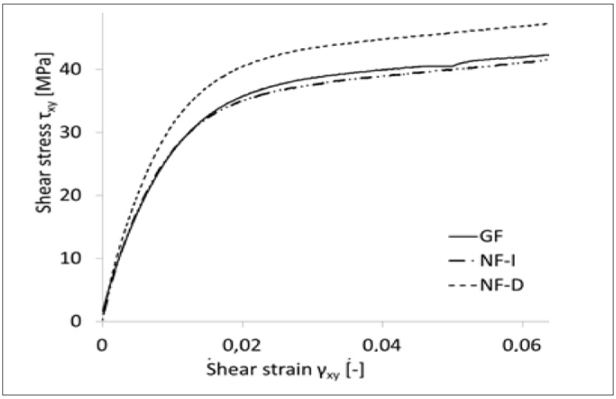

Figura. 2 Shear for [-45°,+45°]2s

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CONTENTS

DEVELOPMENT AND CHARACTERIZATION OF BIOACTIVE *Β*-LACTOGLOBULIN NANO-HYDROGELS FOR FOOD APPLICATIONS

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INTRODUCTION

Whey proteins produced during bovine cheese manufacture, or membrane fractionation of bovine milk account for increasingly valuable food ingredient – owing to their nutritionally-balanced composition in amino acid residues coupled with their functional properties (e.g. solubility, and gel-forming, emulsifying and foaming features)[1]. β-Lactoglobulin (β-Lg) is the major fraction of bovine whey proteins (i.e. 50 wt%), and a primary gelling agent; it is stable at low pH and highly resistant to proteolytic degradation in the stomach, besides its ability to act as encapsulating agent[2].

OBJECTIVE

The objective of this work was to understand the kinetics of aggregation during heat treatment, under narrow pH ranges, that leads to the formation of edible β-Lg nano-hydrogels as well as to rationalize the contribution and importance of covalent and noncovalent interactions to maintain the structure thereof. Furthermore, the ability of said nano-hydrogels to encapsulate bioactive compounds (e.g. vitamins) was also assessed.

MATERIALS AND METHODS

In this study, aqueous dispersions of β-Lg were accordingly produced, and formation of stable β-Lg nano-aggregates was ascertained after heating at different temperatures (i.e. 75, 80 and 85 ºC), for different holding periods (i.e. 5, 10 and 20 min) and under different pH values (i.e. 4, 5, 6 and 7); particular emphasis was on pH 6.0. The protein aggregates formed were characterized for stability (turbidity), role of covalent or non-covalent bonds, surface hydrophobicity, morphology, size, surface charge, and content in accessible thiol groups.

RESULTS

Stable dispersions of β-Lg nano-hydrogels were obtained at pH 6, corresponding to an aggregation yield of ca. 65, 77 and 92%, at 75, 80 and 85 ºC, respectively – for a holding period of 20 min. Such structures were characterized by particle size between 100 and 160 nm, low degree of polydispersity (<0.2), and an association efficiency of vitamin B_2 above 50%. Their ζ-potential varied from +20 to -40 mV, depending on pH. Nano-hydrogels obtained at pH 5 displayed a lower content of accessible thiol groups as compared to those obtained at pH values above or below. For pH between 4 and 5, large sedimenting protein particulates were obtained, whereas soluble aggregates were formed at pH values outside that range.

Acknowledgements

The authors Óscar L. Ramos and Ricardo N. Pereira are recipients of a fellowship (SFRH/BPD/80766/2011 and SFRH/BPD/81887/2011, respectively), supported by Fundação para a Ciência e Tecnologia, POPH-QREN and FSE (FCT, Portugal). The support of EU Cost Action MP1206 is gratefully acknowledged.

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FUNCTIONALIZATION OF ELECTROSPUN NANOFIBERS VIA DIELS-ALDER “CLICK” REACTION

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Polymeric nanofibers are promising candidates for biomedical applications due to their high surface to volume ratio, tunable porosity, controllable scaffold composition and physical resemblance to the fibrillar structure of extracellular matrix [1]. However, these materials usually lack appropriate functional groups which would help to guide specific biological functions [2]. In general, time and resource consuming methods such as plasma treatment, surface graft polymerization, and coelectrospinning of growth promoting (bio)molecules are used for the functionalization of nanofibers, as functionalization is highly desired to improve the properties of synthetic biopolymers such as biocompatibility, cell-adhesivity, stimuli-responsivity for drug delivery [3,4]. A recent study of Becker group showed that click chemistry is a convenient method for the functionalization of nanofibers under mild conditions [5].

In the present study, we investigated the electrospinning of clickable nanofibers which can be easily functionalized using the Diels-Alder reaction at room temperature. At first, we synthesized reactive copolymers which contains furfuryl methacrylate as the reactive group for functionalization, poly(ethylene) glycol methyl ether methacrylate side chains for anti-biofouling and methyl methacrylate to increase the hydrophobicity and fiber-producing propensity. Nanofibers were produced from this copolymer using the solution electrospinning method and the effects of electrospinning parameters on the fiber diameter were studied. Then, reagent-free (bio)functionalization of the furan-reactive nanofibrous scaffolds with maleimide-appended molecules and ligands using the Diels-Alder chemistry was demonstrated.

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CONTENTS

AMPHIPHILIC FLEXIBLE LONG SIDE CHAIN GLYCOPOLYMERS AND THEIR USE AS STABILIZER FOR EMULSION POLYMERIZATION

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INTRODUCTION

Carbohydrate binding proteins present on the cell surface act in transmitting information through recognition processes triggering some cellular responses such as cell proliferation[1] or pathogen infections[2]. In this context the glycopolymer technology is opening new opportunities in many biological and biomedical applications and has as advantage their higher protein-glycopolymer interactions due to the multivalent effect of clustered carbohydrate, the so-called ''glyco-cluster effect''[3,4]. These reasons have motivated the preparation of synthetic composition defined-glycopolymers containing pendant carbohydrates. In the present work synthesis of statistical glycopolymers is described and also the preparation of functionalized polymer latex particles and their corresponding coatings by using these glycopolymers as surfactants in emulsion polymerization.

RESULTS AND DISCUSSION

A novel glycomonomer was synthesized from poly(ethylene glycol) methacrylate (PEGMA). The procedure, already reported for 2-{[(D-glucosamin-2-N-yl)carbonyl]oxy}ethyl methacrylate (HEMAGl)[5], involves activation of terminal hydroxyl moieties with ester groups and subsequently incorporation of glucosamine forming amide linkages. The obtained glycomonomer (PEGMAGl) was copolymerized with methyl acrylate by free radical polymerization varying the initial feed composition to produce amphiphilic glycopolymers which subsequently were characterized compared with their homologous based on HEMAGl.

Both series of copolymers were used as surfactants in emulsion polymerization showing good results as emulsifiers providing stable and monodisperse latex particles between 200 to 400 nm in size. However, the PEG flexible chain has a great influence on the properties of that glycopolymer. This spacer increases the overall hydrophilicity of the copolymers and then less amount of carbohydrates is needed to obtain water soluble compounds and smaller particles sizes are obtained. Besides, the glass transition temperature of the glycopolymers considerably diminishes and, consequently, the later film formation process from the latex particles is favored (Figure 1).

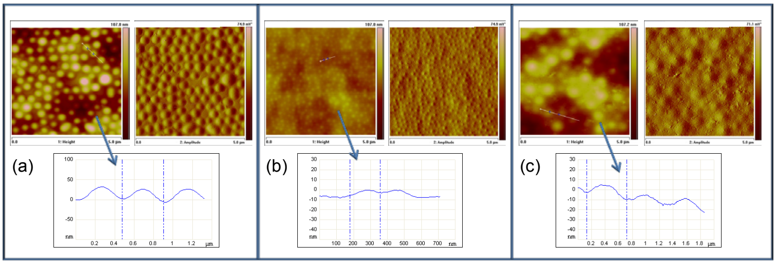

Figure 1. AFM images (height image, its corresponding cross section and amplitude image) of PMA latex with a) HEMAGl based copolymers and b) PEGMAGl based copolymers as surfactants and c) a surfactant-free latex

In addition, bioactivity was evaluated by using the specific carbohydrate-binding lectin Concanavalin A. Films containing PEGMAGl based copolymers showed higher degree of protein binding, as a result of the flexibility required to achieve optimal conformation for binding. Moreover, the same result was obtained when increasing amount of carbohydrate groups in the copolymer composition due to a higher number of available functional groups.

CONCLUSIONS

Amphiphilic copolymers from novel PEGMAGl monomer and methyl acrylate were synthesized at different feed compositions and compared to their homologous HEMAGl based copolymers. The emulsificant capability and the film formation processes were evaluated focusing on the influence of the side chain length and the amount of carbohydrate groups in the copolymer. The results demonstrated the higher is the chain flexibility and the amount of carbohydrate units, the easier is the film formation and the higher lectin binding.

Acknowledgements

M. Álvarez-Paino acknowledges to MINECO for financial support (Project MAT2010-17016) and her FPI grant.

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MICROSTRUCTURE AND THERMAL STABILITY IN METALLOCENE IPP-MATERIALS: TERPOLYMERS WITH ALPHA-OLEFINS

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INTRODUCTION

The precise knowledge of the degradation processes in polymeric materials is mandatory since these might occur during their processing, shelf-life and subsequent recycling. On the other hand, current environmental policies invite the recycling, energy recovery or conversion to avoid excessive consumption of raw materials and waste accumulation.[1]

Studies conducted under inert conditions using pyrolysis allow learning the internal stability of polymeric materials out of contact with oxygen. The pyrolysis takes place in a changing material since evolution of the microstructure occurs along the process. Molecular weight, configuration and chemical nature of the defects within the macrochains are directly connected to the apparent activation energy (E_{act}) of thermal decomposition. This work is focused on the thermal stability of isotactic polypropylene and its terpolymers with 1-pentene and 1-hexene as counits, because of their great number of applications in different industrial sectors.

RESULTS AND DISCUSSION

Synthesis of the different isotactic polypropylenic materials was performed in a stainless steel autoclave. Analytical thermogravimetric measurements were carried out from 40 ºC up to 700 ºC in a TA TGA-Q-500 equipment using 2, 5, 10 and 20 ºC/min as constant heating rates and 50 mL/min as nitrogen flow. Microstructural details (i.e., composition in comonomers as well as the tacticity) were determined by carbon nuclear magnetic reso-

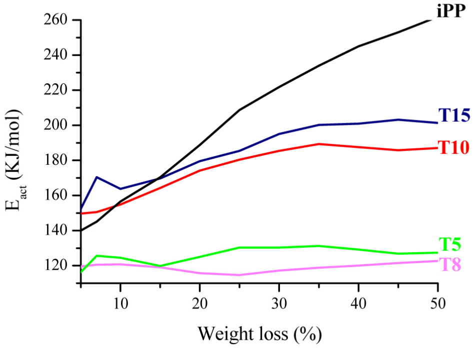

Figure 1. Evolution of the apparent E_{act} for the pyrolisis of the iPP and terpolymers with conversion

nance, ^{13}C NMR using 1,1,2,2-tetrachloroethane-*d*4 (70 mg/1 mL) as a solvent at 80 ºC in an Innova 400 spectrometer (100 MHz).

The Friedman's iso-conversional method has been used to calculate the variation of the E_{act} all along the range of decomposition conversion here analyzed (see figure 1). The trends in weight losses correspond to single step processes. This unique mechanism implies the scission of main-chain bonds and the evolution of the so-generated macroradicals through non-statistical patterns.

Acknowledgements

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EFFECT OF ECM MATERIALS INCLUDED LAYERED NANOFIBERS ON CELLS PROPAGATION

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INTRODUCTION

Polymer nanofibers are promising structures for use as tissue scaffolds [1, 2]. Nanofibrous materials produced by electrospinning have a combination of unique properties that mimic the extracellular matrix [3], however it is possible to enhance their efficiencies in cell culturing by directly incorporating ECM materials into the nanofibers. In this study with the intention of testing the effects of the material composition and layering of nanofibrous materials, we chose a potential adipose tissue reconstruction model using 3T3-L1 mouse fibroblast cells. In order to improve typical polymer nanofibers for use as tissue scaffolds, we incorporate (matrigel, fibronectin, and collagen) into PCL nanofibers and compare cell proliferation over a designated time using various combinations of the different ECM materials. We also compared single layer and double layer scaffold constructs.

RESULTS AND DISCUSSION

We began by electrospinning PCL and the ECM materials in various combinations and characterizing the resulting fibers using SEM. Analysis revealed that both concentrations of ECM materials and combinations of two and three were successfully incorporated into electrospun nanofiber scaffolds. In order to verify the viability of the cells on the nanofiber mat structures, DAPI staining and Live/Dead staining tests were performed. To support our qualitative findings, we also performed statistical analysis. According to the results, better cell propagation was obtained with the triple combination of ECM materials incorporation. In case of layering, double layering worked better in cell culturing studies than single layering. Solvent based studies revealed that HFIP solvent is better working than the mixture of DMF/Chloroform solvent system.

CONCLUSIONS

In this study we proved that introducing 3T3-L1 cells into double layered nanofiber mats including triple combination of matrigel, fibronectin, and collagen (MFC) materials give us better cell proliferation rate when compared to single layered nanofiber mats having cells seeded on top of mats.

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AN ECO-FRIENDLY CONDUCTIVE SENSOR BASED ON BIODEGRADABLE FIBRES OF PANI/PHB

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ABSTRACT

Electrospinning seems to be the most suitable technique to obtain long polymer fibres of submicron diameters. This technology is mostly suitable whenever the high surface area to volume ratio is required, e.g. in highly efficient filtering materials, scaffolds for tissue engineering, nano-chemical sensors, etc. In the latter case, nanofibrous interacting layers enhance the available sensing surface area, providing an increase in sensitivity and capture efficiency, due to surface area approximately one or two orders of magnitude higher than in continuous films. Among electrospun conductive polymer (CP) sensors, polyaniline (PANi) has been one of the most investigated solid state materials due to both its environmental stability (up to 300°C) and peculiar sensing mechanisms. For instance, a dedoping effect through deprotonation is expected to happen when ammonia gaseous is adsorbed onto PANi molecules. On the contrary, acidic gases (HCl, H_2S, and CO_2 with water) cause PANi doping through protonation. In addition, volatile organic compounds (VOCs) change conductivity of the solid state polymer. Each of these events upon polymer exposure to analytes can be measured as current variations detectable through suitable resistors [1]. Electrospun blends of PANi and insulating host polymers (HPs) have been designed, prepared and studied in our laboratory to assess the sensing features of nanofibres resulting from the combination of CP electrical conductivity and HP physical properties [2]. In order to create a new generation of environmental friendly sensors, a biocompatible and biodegradable nanofibrous sensor based on PANi and poly-3-hydroxybutyrate (PHB) was fabricated, characterized and tested to detect VOCs and gases. Specifically, the interdigitated electrodes (IDEs) coated with 10 min electrospun fibrous layers at increasing concentrations of PANi, were investigated through optical microscopy, SEM, AFM and TEM. All layers were highly porous, with interconnected void volumes and high surface-to-volume ratios. Additionally, the polymeric fibres covered both all electrodes in each IDE and the gaps between them, providing electrical connection within each transducer. The sensor retained good mechanical integrity and thermal stability until six months, at least, which reflected into reproducible sensing properties, and it was water resistant. All sensors fabricated at different PANi concentrations resulted conductive and fast responding to gases (NH_3, NO_2) and VOCs (acetone, acetic acid). The amount of PANi in nanofibres was a key factor for layer conductivity (low noise, increase in current), dependence on environmental parameters (humidity, temperature) and interaction with gases and VOCs.

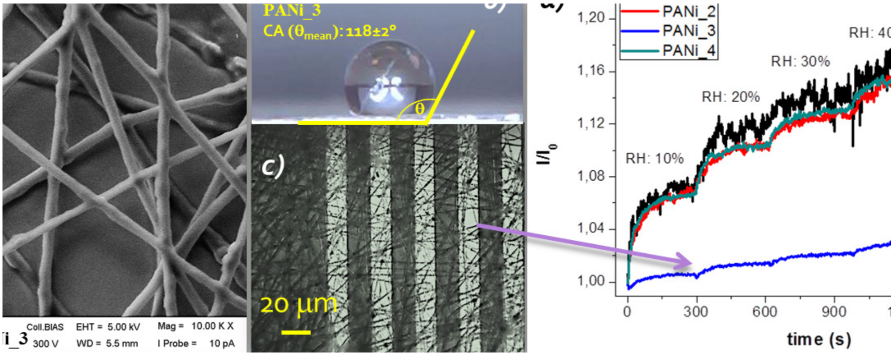

Figure 1. a) SEM micrograph of PANi/PHB (termed as PANi_3 [4.5 10^{-4} M]) electrospun fibres deposited on an oxidized silicon wafer; b) water contact angle of electrospun PANi_3 and c) optical micrograph of an interdigitated electrode coated with the same fibres; d) current changes of PANi/PHB sensors with 4 different concentrations of PANi (increasing from PANi_1 to PANi_4, respectively) when water vapour percentages were flowed through the measurement chamber housing the sensors

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USE OF ELECTROSPINNING FOR ENCAPSULATION APPLICATIONS

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INTRODUCTION

The development of micro- and nanostructures from biopolymers for encapsulation applications is an emerging area of interest in a number of fields such as biomedicine, food technology, energy storage, etc. Apart from the conventional microencapsulation techniques, such as spray drying or coacervation, electrospinning has been recently suggested to be a simple method to generate submicron capsules for a variety of molecules[1, 2, 3]. The electrospinning process uses high voltage electric fields to produce electrically charged jets from viscoelastic polymer solutions which on drying, by the evaporation of the solvent, produce ultrathin polymeric structures[4]. Some interesting characteristics of the technique are that no temperature is required and that an enhanced control over the size distribution of the capsules can be achieved.

RESULTS AND DISCUSSION

Energy storage applications: Phase Change Materials (PCMs) are able to absorb and release a large amount of energy during their phase transition process over a narrow temperature range. Thus, the encapsulation of PCMs can be used to enhance the energy storage capability of different materials. Figure 1 shows the SEM image and the DSC thermogram of zein/PCM capsules. It was observed that the material provided ca. 30 J/g at -10 ºC. The use of these capsules in the food packaging materials or in the walls of refrigeration equipments can buffer thermal variations and improve the quality and security of foodstuffs[3,5].

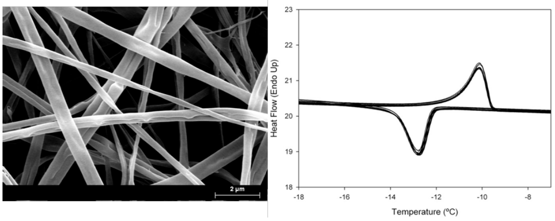

Figure 1. SEM image (left) and DSC thermogram (right) of zein/PCM capsules

Nutraceutical applications: The encapsulation of nutraceutical ingredients seeks to protect these products from adverse conditions and, thus, assure their health-promoting properties. Organic solvents may be even prohibited for these applications, thus electrospinning from aqueous solutions should be carried out. That issue further complicates the electrospinning process due to several factors. Nevertheless it can be achieved through the addition of surfactants[6]. Figure 2 shows SEM images of maltodextrin electrosprayed capsules obtained from aqueous solutions. It was observed that the addition of surfactants allowed the formation of ultrathin capsules. This was mainly due to a reduction in the surface tension caused by surfactant addition.

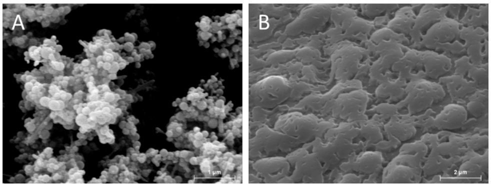

Figure 2. SEM images of maltodextrin capsules with (A) and without the surfactant (B)

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BLOCK COPOLYMERS IN ORGANIC SOLAR CELLS

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The drive to remove mankind's on fossil fuels, while maintaining stable energy supplies, is of vital importance in the coming decades due to the degradative effects of CO_2 production on the Earth's atmosphere. Solar energy is seen as a major contributor to solving these problems; harnessing even a small percentage of the incident solar flux would more than meet total global energy demands.[1] There are a number of solar capture technologies available; herein the advantages and disadvantages of organic photovoltaic (OPV) technology will be discussed.

Figure 1. Flexible, lightweight, thin film organic photovoltaic device

OPV is an inexpensive, clean and renewable energy source, and is an extremely promising option for replacing fossil fuels. It is expected to deliver printable devices processed on flexible substrates using high-volume techniques (Figure 1). Such devices, however, are currently lower in efficiency (than conventional silicon-based technologies) and lack the long-term stability to allow organic photovoltaics to surpass current technologies. Block copolymers are envisaged to help overcome these obstacles because of their long term structural stability (prevention of large scale phase segregation) and their solid-state morphology being of the appropriate dimensions to efficiently perform charge collection and transfer to electrodes.

Herein, the field is discussed and the latest polymers from our group are presented and explored in terms of synthesis, self-assembly and device performance.[2,3]

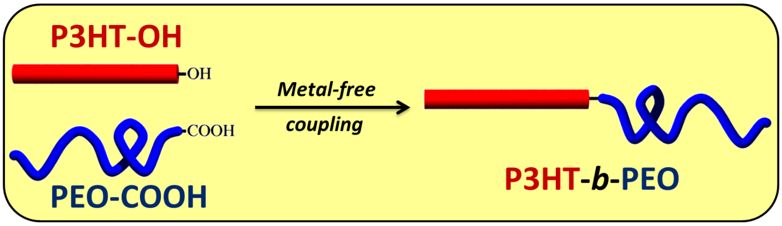

Figure 2. OPV-relevant block copolymer synthesised via simple, metal-free coupling chemistry with high yield[3]

Acknowledgements

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CRYSTAL MORPHOLOGY OF POLYAMIDE NANOFIBRES ANALYSED USING FAST-SCANNING CALORIMETRY

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INTRODUCTION

Understanding and controlling the crystal structure of polymers is crucial to gain insight in mechanical, chemical and thermal properties of finished polymer products [1]. Thermal analysis plays a major role in this characterization, with differential scanning calorimetry (DSC) as one of the most popular techniques. At heating rates of about 10-20 °C/min, the crystal structure is often changing. As a result the melting peak observed is often not representative for the initial crystal structure. In recent years, several forms of fast-scanning calorimeters (FSC) have been developed [2], expanding the possibilities to study polymorphous materials. This paper presents the importance of heating rate in thermal analysis to study the morphology of oriented polymorphous structures such as polyamide (PA) nanofibres.

METHODS

The thermal properties of electrospun nanofibres of three PA types (PA6, PA46 and PA69) were measured using a fast-scanning calorimeter (Rapid Heat-Cool DSC or RHC, TA Instruments). The RHC cell, about 6 mm wide, is heated by four quartz halogen lamps with an almost instantaneous response, overcoming the problems for applying high heating rates with conventional resistive heaters. Scan rates from 20°C/min to 1000°C/min were tested.

RESULTS AND DISCUSSION

During the production of nanofibres by electrospinning, a substantial elongation takes place, inducing orientational order of the polymer chains [3]. This has a significant influence on the crystal structure: all PA types show a more stable crystal morphology (higher T_m) in nanofibres compared to bulk material (Fig. 1). The difference in melting behaviour, however, is most clearly visible when high heating rates are used (Fig. 1b). This is especially the case for PA69, since the low-melting crystal phase is not visible at 20°C/min. The amount of low-melting phase is much smaller in nanofibres than in bulk (15% vs. 71%). At 20°C/min, a small recrystallization peak of the bulk material indicates the reorganization of a low-melting phase, but it is not quantifiable. Fast heating suppresses kinetic processes such as cold crys-

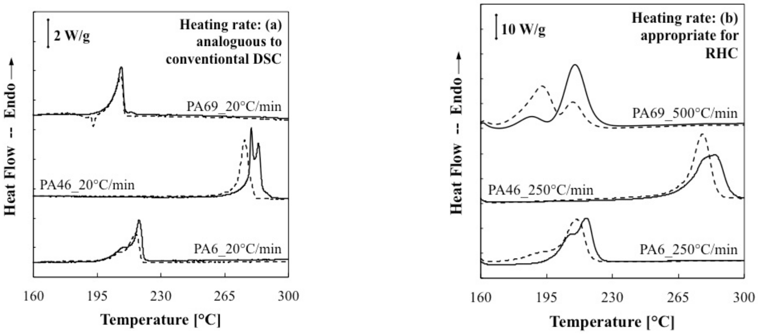

Figure 1. Melting of PA nanofibres (full lines) and bulk material (dotted lines) as a function of heating rate (a vs. b)

tallization, crystal reorganization and crystalline perfectioning, which can be necessary for a correct analysis of the crystal structures formed during processing. However, high heating rates may result in a reduced resolution, as can be seen for PA46 (Fig. 1a vs. 1b).

CONCLUSION

Analysis of the crystal structure in PA6, PA46 and PA69 nanofibres using RHC showed that a correct choice of scan rate is crucial. Finding the golden mean between suppression of kinetic processes and limitation of thermal lag is key and a comparison of the melting behaviour at high and low heating rates is recommended. Applying this method, our results indicate that nanofibres have a crystal structure with higher thermal stability compared to bulk material, which can be ascribed to the high degree of stretching during the electrospinning process. RHC thus offers the possibility of a more rigorous thermal characterization of complex structures such as highly oriented polymorphous nanofibres.

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THE INFLUENCE OF THE INITIATOR/FILLER WITH DIFFERENT FUNCTIONALITY ON THE PROPERTIES OF SYNTHESISED POLY(LACTIDE)

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New biomaterials prepared from natural resources have provided significant opportunities and progress in medicine and pharmacy, which make additional challenges to create biomaterials with specific properties. The topology of biodegradable polyesters can be adjusted by incorporating multifunctional monomers into the polyester backbone to obtain branched polymers. In this work was investigated the influence of multifunctional monomers or fillers, acting as initiator, on the properties of synthesised poly(lactide), PLA. The final properties of the resulting PLA based star shaped polymers can be adjusted by choosing the respective chemical structure of core, depending on the required application. Star branched polyester polyol was obtained by lactide polymerization, using, as an initiator, castor oil that has functionality higher than 2. The molar architecture of biodegradable PLA polymers also was adjusted by incorporating, di-functional monomers into the polymer chains in order to obtain desired properties of final materials. When incorporates some cyclic monomer (such as isosorbide) in flexibly polymer chain glass transition temperature should be increase due to rigidity of copolymer chain. Even a rather low content of isosorbide (one molecule in PLA chains) has a significant influence on the thermal properties raising the Tg and the T_m values. Therefore, incorporation of isosorbide into PLA allows fine-tuning of the thermal properties of this very important biodegradable polymer.

To investigate the influence of multifunctional filler on the properties of PLA high performance composites, a series of multiwall carbon nanotubes (MWCNT)/PLA composite, with different contents of functionalised MWCNT were synthesized via solution ring-opening polymerization of lactide in the presence of trifluoromethanesulfonic acid as catalyst. Composite was synthesised by the “grafting from” method facilitates growth of the poly(lactide) chains from the surface of the functionalized MWNT by reaction between the surface functionalities of the nanotube with the lactide monomers. The modifications of MWCNT were achieved in chemical reaction with strong acids, introducing chemical groups on the surface and by using high energy irradiation technique. FTIR analysis confirmed that ring opening polymerization (grafting) of lactide, in controlled condition, is possible to perform from the surface of functionalised MWCNT. Even a rather low content of f-MWCNT had a significant influence on the thermal properties raising the Tg and the Tm values of obtained PLA nanocomposites. A SEM image demonstrates that the MWCNT was completely coated by the PLA layer, and that the diameter of the coated MWNT (~30 nm) was larger than that of the pristine MWCNT (~15 nm). This suggests a strong interaction between the MWNT and grafted PLA chains. The individual tubes were obviously separated from each other due to PLA covering and such “rods” were glued together. This indicates that the lactide ring opening polymerisation reaction took place over the whole surface of the functionalised MWCNT.

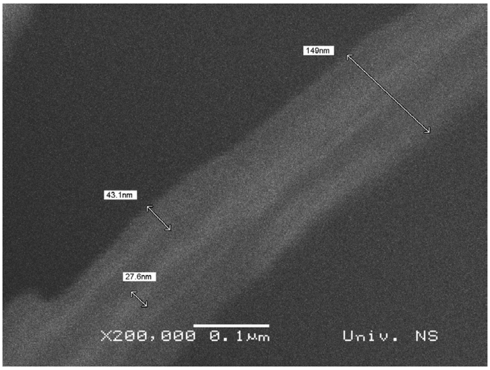

Figure 1. SEM image of MWCNT/PLA nanocomposite

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CONTENTS

THE USE OF COMPLEX MAGNETIC BIOMATERIALS FOR BACTERIAL BIOFILM REDUCTION

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The formation of bacterial biofilms in filtration devices has significant negative economic effects. *Pseudomonas aeruginosa*, an opportunistic human pathogen, is often chosen as a model microorganism for biofilm formation. Biofilm formation is regulated through quorum sensing (QS) in response to bacterial population density, by producing, releasing and detecting small, signalling molecules, such as acylated homoserine lactones (AHLs) in Gram-negative bacteria. In the case of *P. aeruginosa, N*-(3-oxododecanoyl)-L-homoserine lactone and *N*-butanoyl-L-homoserine lactone are utilized as signalling molecules. The enzymatic degradation of AHLs, a technique employed by a diverse group of organisms, disrupts QS, a process referred to as quorum quenching (QQ). Four types of enzymes have been shown to possess the ability to degrade AHLs: AHL-lactonases, decarboxylases, AHL-acylase and deaminase.

The aim of this study was to generate a simple procedure for the immobilization of QQ-enzyme producing bacteria into biopolymers to decrease biofilm formation in water environments. Several biopolymers (i.e. chitosan, alginate, polyvinyl alcohol), and their conjugates, together with magnetic iron oxides particles were tested as a matrix for cells immobilization. The magnetically responsive complexes were examined for QQ enzyme activity and stability in experimental conditions. *P. aeruginosa* biofilm formation was assessed using crystal violet staining assays.

Of the biopolymers tested, alginate was the most successful candidate for the cells immobilization. Moreover, depending on the strain of QQ-enzyme producing bacteria, biofilm formation can be decreased by over 50%. The whole cell biocatalyst can be easily separated out of solution using the magnetic properties of the complex. These results suggest that

BIOPOLYMERS IN SEAFOOD PACKAGING. THINFISH PROJECT

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INTRODUCTION

Non cooked fish packaging industry is gaining more and more importance as result of the fast development of this market, both in terms of volume and complexity, in which packaging plays a major role as a means of food preservation. The non-cooked fish sector uses around 2.000 millions of packages annually. The main requirements of these packages are oxygen barrier, safety and full recyclability. Currently, a wide range of materials such as metal, glass or plastic are used.

Plastics are the most versatile materials as regards to low weight, customized design, low cost… Actually, accomplishing many applications requirements can only be met by combining several plastics into a multilayer structure that reduces their recyclability and increases the final packaging cost. Moreover, the manufacture of these packages often leads to lots of scrap production and design limitations. Related to this, the growing demand from consumers and legislators for less waste and more environmental protection are increasing the necessity for polymeric materials satisfying the conditions of biodegradability, biocompatibility and release of low-toxicity degradation products, as an alternative to conventional polymers. Unfortunately, the lack of commercially acceptable performance of fully biodegradable polymers available until now has blocked the replacement of the traditional non-degradable plastics in the market.

In this context, the Technological Institute of Plastics - AIMPLAS and the National Association of Fish and Seafood Canning Manufacturers – ANFACO, together with the Spanish company CRIIMPLA, coordinator of the project, and the Bulgarian company AKUMPLAST, have started the THINFISH project. The objective is to industrialize and optimize a new technology that will result in an innovative fish package made of polypropylene and wheat starch, which will be recyclable and biodegradable.

RESULTS AND DISCUSSION

THINFISH project pretends to industrialize the technologies related to the adaptation of a gas barrier, competitive cost, recyclable and thin package obtained by co-injection moulding process, for non-thermally seafood products, using as a core layer a non-chemically treated thermoplastic wheat starch and polypropylene (PP) as skin layer. Destructurized wheat starch, is soluble in water and allows the complete separation of both materials, skin (PP) and core (starch), thus recycling 100% the package´s skin (PP).

Firstly, different packages and seafood products have been selected to evaluate the new THINFISH recyclable package. After analyzing all candidates, pickled anchovies packed in a polypropylene package have been chosen as the package-foodstuff combination with the best chance of success. The chosen design has been fully characterized using different CAE programs in order to evaluate its processability using the co-injection technology and its mechanical behaviour during transport and storage. According to the results obtain in the simulation and taking into account the different technologies that exist in the market, simultaneous co-injection technology has been selected. Once the technology has been selected, the prototype and multicavity mould is going to be manufactured.

Besides, simulation of the compounding process, the optimization of the compound formula and the characterization of the developed compounds have been accomplished. New compound has been produced and characterized to generate data for compounding and injection moulding simulation software. Once the different moulds are made will carry out the tasks concerning co-injection process at industrial level, characterization and validation of final packages, and analysis of its behaviour during the packaging process and its useful life.

Acknowledgements

The THINFISH project is funded by the Executive Agency for Competitiveness and Innovation (EACI), within the call CIP-EIP-Eco-Innovation-2011.

TOP-DOWN APPROACH FOR THE PREPARATION OF BIODEGRADABLE PLLA MICRO-CYLINDERS WITH HIGHLY POROUS SURFACE MORPHOLOGY

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INTRODUCTION

Anisotropic micro and nano-particles have been emerging as promising tools in a wide range of sophisticated biomedical applications, going from site-selective intracellular drug/gene delivery[1] to probes to visualize dynamic processes in living cells[2], tumor cell "killers"[3] and tissue engineering scaffolds[4]. The success of the application is strongly related to the surface properties of the particles, which play a key role in governing the primary interactions between the biomaterial and the biological surroundings[5,6]. Here, we present a feasible method to control the surface morphology of biodegradable PLLA micro-cylinders produced by aminolysis of electrospun membranes.

MATERIALS & METHODS

Electrospinning, aminolysis, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), Orange II dye assay.

RESULTS

Electrospinning of PLLA dissolved in a highly volatile solvent, such as dichloromethane (DCM), results in fibers with a high superficial porosity. We show that simply by aminolysis it is possible to break up the PLLA electrospun membrane into micro-cylinders, without significantly affecting the morphology of the surface, which consists of an ordered array of oval submicropores. As confirmed by DSC and XRD measurements, the mechanism of formation of the porous micro-cylinders can be understood as a balance between a solvent-induced lamellar crystallization and the preferential cutting in the amorphous regions of the fiber. As a consequence the fiber will break in the perpendicular direction while the surface erosion is limited (Fig.1). The aspect ratio and the average molecular weight of the PLLA micro-cylinders are inversely proportional to the aminolysis time. More importantly, in our experimental

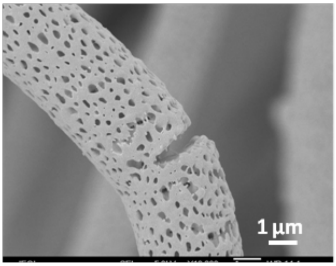

Figure 1. SEM image of PLLA electrospun fibers after 1h aminolysis

conditions, the reaction of aminolysis is expected to introduce free primary amine funcrionalities on the surface of the particles, which we quantified by Orange II dye assay.

CONCLUSIONS AND FUTURE PERSPECTIVES

We presented a method to prepare PLLA micro-cylinders of highly porous surface morphology by aminolysis of electrospun membranes. The surface morphology in turn influences the amount of surface grafted primary amine groups, which can be then easily functionalized. The combination of the nanostructured surface morphology and the free primary amine functionalities on the surface makes our PLLA micro-cylinders ideal candidates for drug delivery applications and as building blocks for new composite biomaterials.

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IMPROVING THE PROPERTIES OF HEAT-INDUCED WHEY PROTEIN HYDROGELS PRODUCED UNDER THE EFFECTS OF MODERATE ELECTRIC FIELDS

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INTRODUCTION

Research on whey utilization is now being largely focused on exploiting their physiochemical and bioactive properties. Whey protein isolate (WPI) is among the most important whey-derived ingredients and consists of products purified to a high protein content (> 90%). The denaturation and aggregation kinetic behavior of WPI upon heating is of particular relevance; when properly engineered and controlled, it results in the production of novel nano-structures with many potential uses in food formulations (i.e. enhancement of textural properties, action as stabilizing agents and delivery of biologically active substances). Combination of heat and moderate electric fields (MEF) treatment interferes with unfolding and aggregation pathways of whey biopolymers [1].

OBJECTIVE

The objective of this study was to induce thermal aggregation of a liquid dispersion of WPI into a three-dimensional network, a so called hydrogel, through combined application of heating and electrical treatment (MEF).

MATERIAL AND METHODS

WPI dispersions (3 % w/v and pH=3) were heated with and without presence of MEF treatments (3 and 10 V/cm) at temperatures of 90 °C. After a heating come-up-time (CUT) period (to raise the temperature from 25 ºC to 90 ºC) the treatment temperature and electric field applied were held constant (holding) for 5 min. Nanostructures and nano-scale phenomena of the initial steps of whey protein aggregation as affected by the applied electric field were assessed by nano-tracking analysis (NTA) and dynamic light scattering (DLS) techniques. Treated WPI hydrogels were analyzed under steady shear flow using a controlled stress rheometer with concentric cylinder geometry in order to assess the effects of MEF on macroscopic properties of the hydrogels produced.

RESULTS

Extent of aggregation decreased with increasing MEF intensity applied, being the onset of gel formation characterized by a polimodal distribution in all treatments; during the first 2 minutes of heating at 90 ºC, MEF treatments applied at 0, 3 and 10 V/cm have determined average mean particle sizes of 156.9 ± 10.7 nm, 141.1 ± 12.9 nm and 117.7 ± 7.8 nm, respectively. From the rheological measurements follows that hydrogel formed under high electric field shows a low apparent viscosity values at high shear rates (see Figure 1). In conclusion, MEF induces changes from a nanometer to macromolecular range thus offering a great potential to the development of WPI hydrogels with diverse mechanical and microstructual features.

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EVALUATION OF ARABINOXYLAN OLIGOSACCHARIDES ON PHYSICOCHEMICAL PROPERTIES OF CHITOSAN BASED FILMS

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Hemicelluloses are known to have good gas barrier properties, making them of huge interest for edible film applications. They are obtained from renewable and worldwide available materials, mostly from biomass residues, often low cost sources. Focusing on the decrease of accumulation of non-degradable packaging waste and the use of natural resources, the utilization of hemicelluloses extracted from agricultural residues for film production is an interesting emerging field [1, 2, 3].

The aim of this work was to evaluate the physico-chemical properties of films formed with chitosan and different arabinoxylans (AXs). AXs were obtained using five different processes and were used to produce five different films (1, 2, 3a, 3b, 4). The treatments used to obtain the five different AX samples were as follows:

1. by NaOH treatment of destarched wheat bran (DWB), then 100 kDa ultrafiltration
2. by NaOH treatment of enzymatically treated DWB with a xylanase, then 100 kDa ultrafiltration
3a. by xylanolytic treatment of DWB, then 10 kDa ultrafiltration, ground and freeze-dried
3b. by xylanolytic treatment of DWB, then 100 kDa ultrafiltration, ground and freeze-dried
4. by hydrothermal treatment of DWB treated with a xylanase, then ethanol-precipitated.

The incorporation of AXs in the films was previously evaluated using different concentrations of chitosan, AXs, plasticizers and surfactants, in order to understand if they would be miscible and would not influence in the manufacture of films. It led to films with a surface and a thickness relatively equal and smooth in all parts. These preliminary experiments allowed defining a film composition of 1.5 % of chitosan (in 1 % lactic acid solution), 0.5 % of glycerol, 0.1 % of tween 80 and 0.2 % of AXs for all the five samples. Glycerol (plasticizer) and Tween 80 (surfactant) were used to avoid brittleness and to improve the mechanical properties of the films. The self-supporting films were formed by the casting evaporation method, dried at 30 ºC during 60 h. Films with chitosan and without AXs were used as control. Films were characterized in terms of water vapour permeability (WVP), opacity, thickness, moisture content and solubility.

The process that appeared more effective relatively to a homogeneous thickness was the extraction by hydrothermal treatment of DWB previously treated with a xylanase (type 4), with values of 0.105 mm. Concerning the WVP, the film that displayed the lowest values was the type 3b with a value of 3.78 E-07 g (m s Pa)$^{-1}$. Moisture values were between 25 and 30 % for all five studied films and their solubility values were around 1 % (w/w). The films with incorporation of AXs type 4 were more opaque, presenting values of 15.49 %. The lowest opacity was observed in the film with type 2 AXs, presenting values of 6.87 %.

In conclusion, wheat bran AXs can be incorporated into chitosan-based edible films. WVP is increased with the presence of AXs, demonstrating an increase of water affinity of the films. For all the other studied properties, no significative differences with the control were evidenced. Thus, AXs can be successfully added to chitosan-based films and can be used as material for edible packaging.

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