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University of Milan, 15-17 July 2020

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SCIENTIFIC PROGRAM
The congress presentations consist of keynote lectures (KN), invited lectures (IL), oral (OC) and poster communications (P)

Wednesday, July 15th, 2020

09:30	**OPENING CEREMONY**	
		E. Ranucci, University of Milan (I), Congress Chair
		L. Prati, University of Milan (I), Head of the Chemistry Department
*1st Session - **Chairperson: P. Ferruti** and **E. Ranucci**, University of Milan (I)*		
09:50 AM	KN	**D. Díaz-Díaz**, University of Laguna (E). *Polymer adhesives and protective coatings via orthogonal "click" chemistry*
10:30 AM	IL	**M. Lavorgna**, Institute for Polymers, Composites and Biomaterials CNR, Lecco (I). *On the key role of carbonaceous filler distribution for advanced polymer-nanocomposites*
10:50 AM	***Break***	
*2nd Session - **Chairperson: D. Díaz-Díaz**, University of Laguna (E) and **M. Coletti**, TA-Instruments (I)*		
11:00 AM	IL	**C. Capacchione**, University of Salerno (I). *Synthesis of aliphatic polycarbonates from carbon dioxide and epoxides promoted by OSSO-type transition metal complexes*
11:20 AM	IL	**F. Auriemma**, University of Naples "Federico II" (I). *Crystallization, polymorphism, morphology and properties of olefin based di- and multi-block copolymers*
11:40 AM	IL	**D. d'Hooge**, University of Ghent (B). *The amazing world of network polymers and their applications*
12:00 AM	***Break***	
*3rd Session - **Chairperson: C. Capacchione**, University of Salerno (I) and **M. Lavorgna**, Institute for Polymers, Composites and Biomaterials CNR, Lecco (I)*		
12:10 PM	OC	**M. Marcioni**, Polytechnic of Turin (I). *Hydrophobic polyamidoamines: a new class of technological materials?*
12:25 PM	OC	**M. Haris**, TA Instruments (D). *Dynamic mechanical characterization of cured NR/BR compounds: including investigations into the effects of mastication time and different peptizers*
12:40 PM	OC	**D. Meroni**, University of Milan (I). *UV-induced synthesis of polyaniline (PANI)-TiO_2 composites: mechanistic insight and application as sorbent for wastewater remediation*
12:55 PM	**LUNCH**	
*4th Session - **Chairperson: F. Ganazzoli**, Polytechnic of Milan (I) and **A. Manfredi**, University of Milan (I)*		
01:55 PM	KN	**H. Iatrou**, University of Athens (GR). *Nanostructured materials for the controlled drug delivery of anticancer agents*
02:35 PM	IL	**P. Chmielarz**, Rzeszow University of Technology (PL). *Chemistry innovations that will change the world – Reversible Deactivation Radical Polymerization*
02:55 PM	OC	**I. Zaborniak**, Rzeszow University of Technology (PL). *Ultrasonication-mediated atom transfer radical polymerization in miniemulsion for the preparation of precisely-defined complex polymer architectures*
03:10 PM	***Break***	
*5th Session - **Chairperson: H. Iatrou**, University of Athens (GR) and **M. Mella**, University of Insubria (I)*		
03:20 PM	OC	**M. Malavolti**, Vinavil S.p.A. (I). *Miniemulsion techniques to include hydrophobic monomers in water based acrylic polymer dispersions*
03:35 PM	OC	**T. Yoshida**, MCPP Germany GmbH (D). *Innovative & sustainable high barrier solutions for circular economy*
03:50 PM	OC	**P. Petrov**, Bulgarian Academy of Sciences (BG). *Novel block copolymer nanocarriers for enhanced solubilization and sustained release of caffeic acid phenethyl ester*
04:05 PM	OC	**S. Granados-Focil**, Clark University (USA). *Thermo-optically responsive solid-solid phase change materials as passive temperature controlling building enclosures*
04:20 PM	***Break***	
04:30 PM	**POSTER SESSION**	
06:30 PM	**END of SESSION**	

Thursday, July 16th, 2020

***6th Session - Chairperson: E. Ranucci** and **P. Ferruti**, University of Milan (I)*		
09:30 AM	KN	**M. Chehimi**, Institut de chimie et des matériaux Paris-Est - CNRS (F). *Adhesion of polymers to diazonium-modified surfaces*
10:10 AM	IL	**J. Covas**, University of Minho, Guimaraes (P). *The cooling stage in extrusion-based 3D printing techniques*
10:30 AM	***Break***	
***7th Session - Chairperson: N. Tirelli**, Istituto Italiano di Tecnologia, Genoa (I) and **F. Auriemma**, University of Naples "Federico II" (I)*		
10:40 AM	OC	**G. Raffaini**, Polytechnic of Milan (I). *Self-structuring of main-chain and pH-dependent conformation of L-glutamine-based polyamidoamino acid: a molecular dynamics study*
10:55 AM	OC	**S. Elli**, Istituto di Ricerche Chimiche e Biologiche "G. Ronzoni", Milan (I). *MD simulation of the interaction between neuraminidase N1 of the 1918 pandemic influenza virus to sialoglycan*
11:10 AM	OC	**A. Scomparin**, University of Turin (I). *Aminated poly(α)glutamate for the systemic delivery of siRNA to solid tumors*
11:25 AM	OC	**M. Mella**, University of Insubria (I). *Weakly polyelectrolytic surfaces: are there important interactions between ionized and neutral tethered monomers?*
11:40 AM	***Break***	
***8th Session - Chairperson: J. Covas**, University of Minho, Guimaraes (P) and **F. Carosio**, Polytechnic of Turin (I)*		
11:50 AM	KN	**A. Pegoretti**, University of Trento (I). *Thermal energy storage/release with polymer composites and rubbers*
12:30 PM	OC	**E. Passaglia**, Institute for the Chemistry of OrganoMetallic Compounds CNR, Pisa (I). *Incorporation of 2D black phosphorus (2D-bP) in polymer matrices for designing new materials with tuned morphological and spectroscopic features*
12:45 PM	OC	**D. Rigotti**, University of Trento (I). *Development of novel furan-based polyester blends*
01:00 PM	**LUNCH**	
***9th Session - Chairperson: A. Pegoretti**, University of Trento (I) and **P. Chmielarz**, Rzeszow University of Technology (PL)*		
02:00 PM	KN	**T. Vermonden**, University of Utrecht (NL). *Balancing hydrophobic and electrostatic interactions in thermosensitive polyplexes for nucleic acid delivery*
02:40 PM	IL	**N. S. Kehr**, University of Münster (D). *Injectable nanocomposite hydrogels for controlled cell migration and local drug delivery applications*
03:00 PM	***Break***	
***10th Session - Chairperson: T. Vermonden**, University of Utrecht (NL) and **V. Castelvetro**, University of Pisa (I)*		
03:10 PM	IL	**R. Cavalli**, University of Turin (I). *Polymer shelled nanobubbles*
03:30 PM	OC	**M. Geven**, Istituto Italiano di Tecnologia, Genoa (I). *Disulfide restructuring on nanomanufactured polymer particles*
03:45 PM	OC	**A. M. Bossi**, University of Verona (I). *Deformable molecularly imprinted nanogels*
04:00 PM	IL	**N. Tirelli**, Istituto Italiano di Tecnologia, Genoa (I). *Fibrin as a cell matrix. Cell-mediated contraction and other phenomena*
04:30 PM	***Break***	
***11th Session - Chairperson: A. Bossi**, University of Verona (I) and **M. Geven**, Istituto Italiano di Tecnologia, Genoa (I)*		
04:40 PM	KN	**S. Guillaume**, Université de Rennes 1 (F). *Poly(hydroxyalcanoates): stereoregular (co)polymers & biomedical applications*
05:20 PM	OC	**A. Gagliardi**, University of Catanzaro "Magna Græcia" (I). *Zein: a versatile and promising natural polymer for drug delivery applications*
05:35 PM	OC	**W. Celentano**, Polytechnic of Milan (I). *Complex polyester-PEG nanoparticles as drug nanocarriers for targeting malignant brain tumors*
05:50 PM	OC	**L. Izzo**, University of Insubria (I). *Is a molecular "traffic warden" the solution to control drug delivery from polymer-based nanocarriers?*
06:05 PM	**END of SESSION**	

Friday, July 17th, 2020		
***12th Session - Chairperson: L. Falciola**, University of Milan (I) and **J. Alongi**, University of Milan (I)*		
09:30 AM	KN	**A. Gomiero**, Norwegian Research Center (N). *Micro- and nanoplastics in the environment: current knowledge and future trends*
10:10 AM	IL	**M. Malinconico**, Institute for Polymers, Composites and Biomaterials CNR, Pozzuoli (I). *Single use plastics directive: EU policies push plastic industry towards a responsible future*
10:25 AM	IL	**V. Castelvetro**, University of Pisa (I). *Microplastics in the environment: an underestimated or overemphasized problem?*
10:45 AM	***Break***	
***13th Session - Chairperson: M. Malinconico**, Institute for Polymers, Composites and Biomaterials CNR, Pozzuoli (I) and **O. Savard**, Hitachi High-Tech Analytical Science Ltd (UK)*		
10:55 AM	IL	**L. Fambri**, University of Trento (I). *Plastics and polymers in Italian aquatic environments. Survey, monitoring, laboratory analysis and educational aspects*
11:15 AM	IL	**M. Cocca**, Institute for Polymers, Composites and Biomaterials CNR, Pozzuoli (I). *Microplastic pollution from synthetic textiles: quantitative evaluation and mitigation strategies*
11:35 AM	OC	**V. Pasini**, Thermo Fisher Scientific (I). *The fate of micro plastic in Earth environments. A proposed workflow for pollutant detection using Raman and Infrared micro-spectroscopy*
11:50 AM	***Break***	
***14th Session - Chairperson: G. Cappelletti**, University of Milan (I) and **M. Cocca**, Institute for Polymers, Composites and Biomaterials CNR, Pozzuoli (I)*		
12:00 AM	IL	**E. Davoli**, Istituto di Ricerche Mario Negri IRCCS, Milan (I). *Microplastics in deep water: a combined GC-MS and FT-IR approach*
12:20 PM	IL	**S. Federici**, University of Brescia (I). *Mimicking microplastic pollution through more realistic reference materials*
12:40 PM	IL	**M. Paturzo**, Institute of Applied Sciences and Intelligent Systems CNR, Pozzuoli (I). *Microplastics identification via holographic imaging and machine learning*
01:00 PM	OC	**N. Kasmi**, Aristotle University of Thessaloniki (GR). *Solvent-free synthesis of new fully biobased diol monomers through industrially viable approach: Toward new insights into the valorization of vanillic acid-based polyesters*
01:15 PM	**LUNCH**	
***15th Session - Chairperson: A. Dorigato**, University of Trento (I)*		
02:15 PM	IL	**F. Carosio**, Polytechnic of Turin (I). *High performing flame retardant materials from surface nanostructuring of biobased components*
02:35 PM	OC	**O. Savard**, Hitachi High-Tech Analytical Science Ltd (UK). *See what is really happening within your furnaces*
02:50 PM	OC	**A. Beduini**, University of Milan (I). *Homo- and copolymeric polyamidoamines as flame retardants for cotton fabrics*
03:05 PM	OC	**A. L. Davesne**, University of Lille (F). *Radiative heat barriers for the fire protection of polyamide 6*
03:20 PM	***Break***	
***16th Session - Chairperson: F. Ganazzoli**, Polytechnic of Milan (I) and **F. Carosio**, Polytechnic of Turin (I)*		
03:30 PM	IL	**L. Mullen**, Publisher Elsevier (UK). *Materials Today: journals and outreach connecting the materials community*
03:45 PM	OC	**M. Arioli**, University of Milan (I). *Highlights on the degradation of polyamidoamines in water and in soil*
04:00 PM	OC	**N. Toncheva-Moncheva**, Bulgarian Academy of Sciences (BG). *Novel linear amphiphilic polyglycidol/poly(ε-caprolactone) copolymers prepared via "click" chemistry-based reactions*
04:15 PM	OC	**F. Ferruti**, University of Milan-Bicocca (I). *Controlled synthesis of linear polyamidoamino acids and preliminary investigation on their cytocompatibility and application in photodynamic therapy*
04:30 PM	**POSTER AWARD ANNOUNCEMENT AND CLOSING REMARKS**	

KEYNOTES

KN1

Adhesion of polymers to diazonium-modified surfaces

Mohamed M. Chehimi

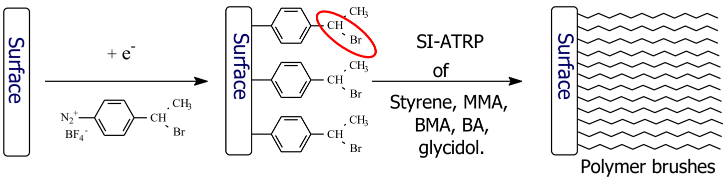
Institut de Chimie et des Matériaux Paris-Est (ICMPE), CNRS and UPEC (UMR7182), F-94320 Thiais, France

chehimi@icmpe.cnrs.fr

Abstract

The surface chemistry of aryl diazonium salts took off in 1992 and progressed since then at a remarkable pace. These salts are known since the mid 19th century in organic chemistry for they permit generating several compounds. The reaction of diazonium salts with materials, particularly carbon, is based on concerted radical grafting mechanisms. True covalent bonding occurs and one can employ the robust arylated materials for numerous purposes such as electrocatalysis, theranostics, reinforcement of polymer matrices and attachment of polymers by in situ, surface-confined polymerization (see Figure 1 as example of surface-initiated ATRP). In this Lecture, the background to surface chemistry of diazonium salts will be briefly summarized and then some of the main achievements from the Lecturer's work and handpicked examples from the literature will be reviewed. In this respect, the focus will be on surface-confined controlled radical polymerization methods (ATRP, RAFT), iniferter, radical photopolymerization and oxidative (electro)polymerization of conjugated monomers, all conducted in the presence of diazonium-modified materials. The applications encompass, sensors based on chelatant polymer and molecularly imprinted polymer (MIP) grafts, diazonium-modified nanofillers for polymer reinforcement, novel TiO_2-polyaniline based photocatalysts. The Lecture will finish by screening emerging trends in the surface chemistry of diazonium salts and new applications in polymer science and engineering.

Figure 1. Example of surface-initiated ATRP using diazonium-modified materials as macro-initiator



KN2

Metal-adhesive polymers via click chemistry

David Díaz Díaz[a,b,c]

[a] Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany

[b] Departamento de Química Orgánica, Universidad de La Laguna, Astrofísico Francisco Sánchez s/n, 38206 La Laguna, Tenerife, Spain

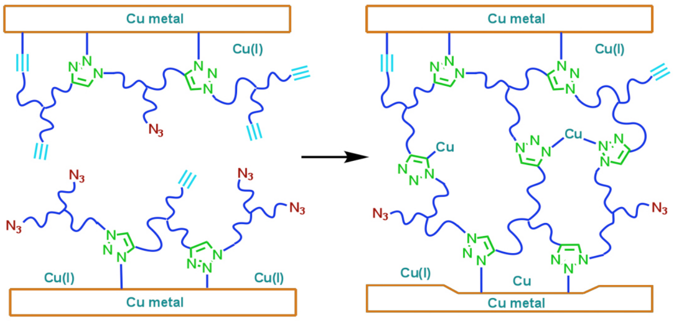
[c] Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna, Astrofísico Francisco Sánchez s/n, 38206 La Laguna, Tenerife, Spain

David.Diaz@chemie.uni-regensburg.de

Abstract

This presentation will describe the use of the cycloaddition reaction between azides and alkynes catalyzed by Cu (I) – prototype of the click chemistry – for the preparation of polymeric materials that work as adhesives for different metal surfaces [1-3]. Copper surfaces, or alloys containing copper such as brass, spontaneously supply the Cu (I) ions necessary for the polymerization reaction that occurs when a mixture of suitable polyvalent monomers comes into contact with the metal surface. In the case of metal surfaces that do not have copper, such as Zn, the copper catalyst can be added to the monomer mixtures before deposition on the metal surface. The adhesive strength of these materials is comparable or superior to the commercial adhesives that usually are employed for these surfaces. Numerous studies on structure-activity correlations have been carried out in order to identify the key properties that influence the strength of the adhesive. This work has allowed the subsequent development of adhesives for other surfaces such as glass, conductive adhesives, and anti-corrosion coatings for different metals such as aluminum [4-7]. It should be noted that the use of click chemistry allows polymerization and adhesion of surfaces to be carried out even under water, which represents an important advance from the standpoint of possible applications of this technology.

Adhesion mechanism of polytriazoles



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KN3

Microplastic and nanoplastics in the environment: current knowledge and future trends

Alessio Gomiero
Norwegian Research Centre AS, Mekjarvik 12, Randaberg, Norway
algo@norceresearch.no.it

Abstract

Plastic litter is a large-scale environmental problem currently receiving global attention. Research into sources, fate and impacts of microplastics has increased exponentially over the last couple of decades. As with any emerging discipline there are more questions than answers. Hence, despite the development of large national and international projects, this field of research is still new, with many unanswered questions. Due to advances in technological development and a pressing research effort, the last decade has seen many studies demonstrating the presence of microplastics across the globe, including remote areas such as the polar regions and the deep ocean. After many groundbreaking descriptive studies there is now a need for robust, rigorous and quantitative science. Continual photochemical and physical fragmentation of plastic items in the environment is expected to generate large quantities of micro to nano sized plastic particles. However, due to technological challenges, the precise quantities of nanosized particles found in environmental samples is yet to be established. From a legislative point of view, it is essential to monitor in order to know whether levels of contamination are changing over time or between locations. Nevertheless, the rationale underlying environmental monitoring is typically to record the concentration or abundance of material considered potentially harmful. Yet we do not know which size fraction is dominant within varying environments, which polymer and which co-occurring pollutants show the greatest or lowest risk. Concerning the potential impact, controlled exposure studies have demonstrated the potential for plastics to transfer chemicals upon ingestion. Nevertheless, there is still uncertainty whether the relative importance of such a pathway is sufficient to induce additional toxicological impair above that resulting from the simple uptake of pollutants from food or water. Furthermore, pioneer exposure studies have been criticized for using exposure concentrations significantly higher than that those observed in nature. However, as more results are becoming available, an underestimation of the actual level of plastic particles in nature is becoming apparent. From a regulatory perspective, an understanding of the thresholds above which a substance might be considered harmful is crucial to set the environmental quality standard for micro & nano sized plastic particles. The lack of information should be not envisaged as a lack of action. On the contrary, concrete acts to reduce the accumulation of plastics in the environment are needed as the release of large plastic items leads to fragmentation into micro and nanoplastics, which will therefore be distributed in the environment for years to come. Undoubtfully, plastic brings many societal benefits, and these could still be realized without emissions of end-of-life plastics to the environment. There is a clear need to reduce and ultimately prevent plastic emissions and to act in a more sustainable manner with regard to the production of single use items. This could be achieved by moving towards a more circular economy, capturing and recycling end of life plastic objects. Successful solutions can only be generated by linking academia, industry and policy to ensure potential actions are evaluated from all perspectives.

KN4

Poly(HydroxyAlcanoates): stereoregular (co)polymers & biomedical applications

Sophie M. Guillaume

Rennes Institute of Chemical Sciences (ISCR), UMR 6226 CNRS - Université de Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes Cedex, France

sophie.guillaume@univ-rennes1.fr

Abstract

Poly(hydroxyalkanoate)s (PHAs) are a class of natural or synthetic aliphatic polyesters which feature the same three-carbon backbone structure, only differing by their substituent (R) in β-position. PHAs have attracted considerable interest as "green" engineering plastics. These biodegradable and biocompatible polymers represent a targeted choice for in particular packaging, and biomedical applications in tissue engineering and as drug delivery systems. Recent highlights of research at Rennes University in the field of 1) tunable catalytic systems for the ring-opening (co)polymerization (ROP) of functional β-lactones (e.g. β-butyrolactone (BL), β-malolactonates (MLA^{CO2R}s; R = CH_2Ph (Bn), $(CH_2)_2{=}CH_2$ (All)), or 4-alkoxymethylene-β-propiolactones (BPL^{OR}s; R = Me, Allyl, Bn)) into their corresponding PHAs (poly(3-hydroxybutyrate) (PHB), poly(alkyl β-malolactonate) (PMLA^{Bn}), poly(alkoxymethylene-β-propiolactone) (PBPL^{OR}), respectively), 2) original sequence controlled PHAs featuring a high degree of control over molecular and microstructural characteristics [1-6], and 3) PHA copolymers as promising drug delivery systems [7,8], will be presented. Our most significant achievements in this endeavor include the development of strategies that enable the synthesis of alternated PHA-based copolymers, and the evidences of the relationship between the catalytic system, the chemical structure and the composition of the macromolecules.

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KN5

Nanostructured materials for the controlled drug delivery of anticancer agents

Hermis Iatrou,[a] Panayiotis Bilalis,[a] Dimitrios Skoulas,[a] Anastasis Karatzas,[a] John Marakis,[b] Athanasios Stamogiannos,[c] Chrisida Tsimblouli,[d] Evangelia Sereti,[d] Efstratios Stratikos,[c] Konstantinos Dimas,[d] Dimitris Vlassopoulos[b]

[a] University of Athens, Department of Chemistry, Panepistimiopolis, Zografou 15771, Athens, Greece

[b] FORTH, Institute for Electronic Structure and Laser, Heraklion 71110, Greece and Department of Materials Science & Technology, University of Crete, Heraklion 71003, Greece

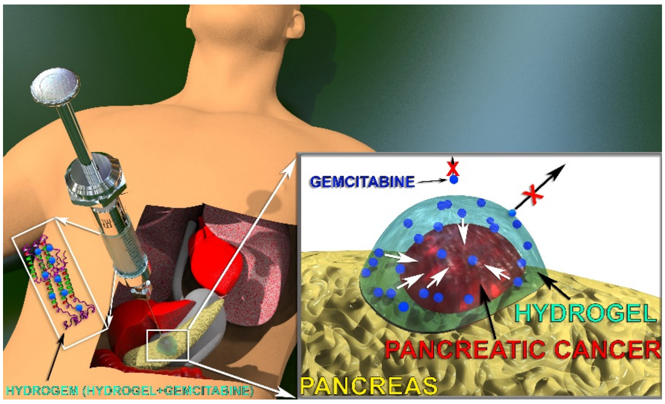
[c] National Centre for Scientific Research Demokritos, Patriarhou Gregoriou and Neapoleos 27, Agia Paraskevi 15341, Athens, Greece

[d] Department of Pharmacology, Faculty of Medicine, University of Thessaly, Larissa, Greece

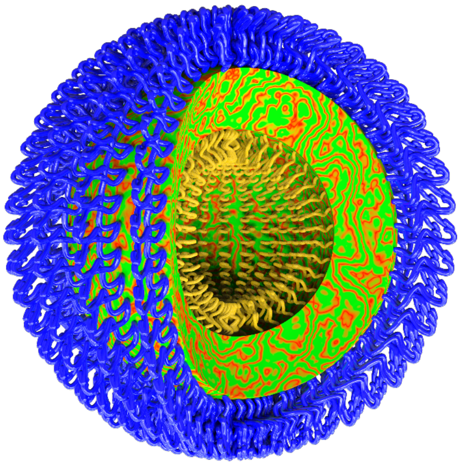
iatrou@chem.uoa.gr

Abstract

A novel, multifunctional hydrogel that exhibits a unique set of properties for the effective treatment of pancreatic cancer (PC), as well as a novel 3-miktoarm star terpolypeptide forming nanoparticles (NPs) in the form of stomatocytes, are presented. The material of the hydrogel is comprised of a pentablock terpolypeptide of the type PLys-*b*-(PHIS-*co*-PBLG)-PLys-*b*-(PHIS-*co*-PBLG)-*b*-PLys. It can be implanted via the least invasive route and selectively delivers gemcitabine to efficiently treat PC. Simply mixing the novel terpolypeptide with an aqueous solution of gemcitabine within a syringe results in the facile formation of a hydrogel that has the ability to become liquid under the shear rate of the plunger. Upon injection in the vicinity of cancer tissue, it immediately reforms into a hydrogel due to the unique combination of its macromolecular architecture and secondary structure. Due to its pH responsiveness, the hydrogel only melts close to PC, thus the drug can be delivered directionally towards the cancerous rather than healthy tissues in a targeted, controlled and sustained manner (a). The efficacy of the hydrogel was tested *in-vivo* on human to mouse xenografts using the drug gemcitabine. It was found that the efficacy of the hydrogel loaded with only 40% of the drug delivered in one dose, was equally or slightly better to the peritumoral injection of 100% of the free drug delivered in two doses, the typical chemotherapy used in clinics so far. These results suggest that the hydrogel can direct the delivery of the encapsulated drug effectively in the tumor tissue [1]. The NPs are formed from the encapsulation of Everolimus with a star-like molecule of the $(A)_2BC$ type, where A is poly(ethylene oxide) (PEO), B is poly(L-histidine-co-γ-benzyl-L-glutamate) (P(His-co-BLG)) and C is poly(L-lysine hydrochloride) (PLL). The NPs are pH-as well as enzyme responsive, and their shape mimic the red-blood cells (b). Both nanostructured materials can be used as drug delivery systems for the targeted delivery of anticancer agents [2].



(a)



(b)

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KN6

Thermal energy storage/release with polymer composites and rubbers

Alessandro Pegoretti, Andrea Dorigato, Giulia Fredi, Francesco Valentini
Dipartimento di Ingegneria Industriale, Università degli Studi di Trento, via Sommarive 9, 38123, Trento, Italy
alessandro.pegoretti@unitn.it

Abstract

Materials with thermal energy storage (TES) capabilities can contribute to a more efficient use of energy. In fact, storing excess heat for a later use can narrow the gap between energy requirement and availability, improve the management of intermittent energy resources and help in regulating the temperature in buildings and electronic devices (thermal management) [1]. Organic phase change materials (PCMs), such as paraffins, which store and release latent thermal energy during melting and crystallization, at a nearly constant temperature are among the most widely used materials for TES. They possess a high energy density and a tunable working temperature, but they need to be confined to avoid leakage when in the molten state. This confinement can be achieved in several manners, i.e. through shape stabilization with nanofiller or layered materials or by micro/nano-encapsulation in inert shells [1,2]. In applications where weight and volume savings are of crucial importance, it is advantageous to embed TES capability directly in the structure. A possibility is to develop multifunctional polymer composites. These permits one to build a multifunctional structure that is also active part of the thermal management system. These structural TES composites can find applications in several fields, such as automotive, building constructions and portable electronics. The activities of this research group have recently focused on developing new polymer composites containing microencapsulated and shape-stabilized paraffins [3]. Several classes of polymer composites have been considered, such as carbon and glass fiber reinforced composites with both traditional (epoxy) [4] and reactive thermoplastic matrices [5], discontinuous fiber composites, elastomers, foams, and filaments for fused-deposition modelling [6]. For example, PCM-enhanced thermoplastic laminates were produced with a novel reactive acrylic resin, Elium$^{®}$ by Arkema, a carbon fiber fabric and microencapsulated paraffin MPCM43D (Microtek, Dayton, OH) with a melting temperature of 43 °C and a melting enthalpy of 200 J/g, in various amounts (20, 30 and 40 wt% of the matrix). The microstructural characterization showed that the PCM phase is preferentially distributed in the interlaminar region (Figure 1), while differential scanning calorimetry (DSC) tests highlighted that the melting/crystallization enthalpy values increased with the capsule content, up to 66.8 J/g.

The considerably high phase change enthalpy was at the basis of the good thermal management performance, measured through thermal camera imaging. These tests consisted in heating the laminates at 70 °C and in measuring the temperature during natural cooling down to room temperature (Figure 2). The plateau-like trends are due to the PCM crystallization, which noticeably increases the time to reach room temperature.

Figure 1. optical microscope micrograph of the polished cross section of an Elium$^{®}$/carbon laminate containing 20 wt% of paraffin microcapsules

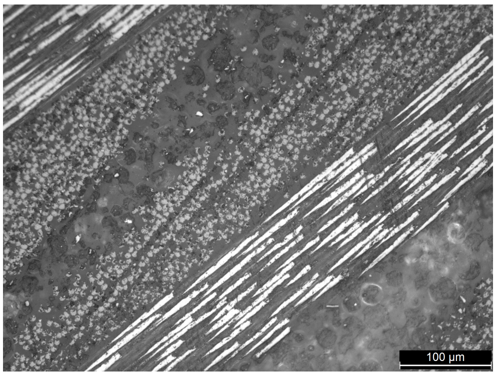
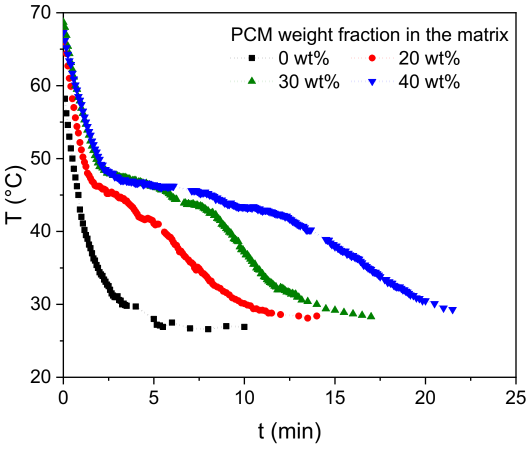


Figure 2. Temperature profiles under cooling for various PCM amounts in Elium$^{®}$/carbon laminates



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KN7

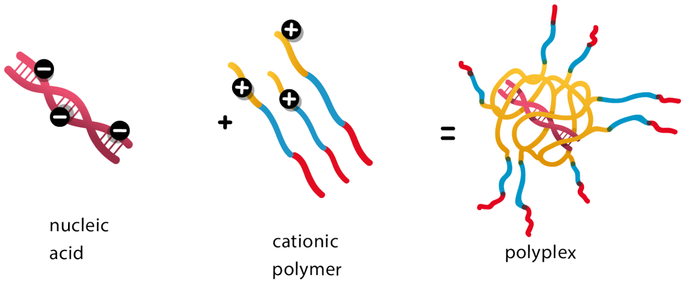
Balancing hydrophobic and electrostatic interactions in thermosensitive polyplexes for nucleic acid delivery

Tina Vermonden, Lies Fliervoet
Department of Pharmaceutics, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherland
t.vermonden@uu.nl

Abstract

Introducing multiple functionalities, like cationic and thermosensitive properties, in a polymer design has acquired attention to improve the efficacy of nucleic acid delivery. Complete condensation of the nucleic acids and the formation of stable complexes are crucial for achieving effective intracellular delivery. Therefore, in this study, the balance between hydrophobic and electrostatic interactions has been investigated for thermosensitive plasmid DNA (pDNA)-loaded polyplexes. NPD triblock copolymers consisting of a thermosensitive *N*-isopropylacrylamide (PNIPAM, N), a hydrophilic poly(ethylene glycol) (PEG, P) and a cationic 2-(dimethylamino)ethyl methacrylate (PDMAEMA, D) block with different block lengths were prepared using a hetero-functional PEG macroinitiator [1]. In this study, we show that there is a critical balance between the electrostatic and hydrophobic interactions between the multifunctional polymer and pDNA at temperatures above the CP. If the length of the cationic block and the N/P ratio are high enough, the electrostatic interactions between the pDNA and the cationic block of the polymer are superior over the hydrophobic thermosensitive interactions, resulting in sustaining the polyplex nanostructure [2]. These results provide new insights into the design of polymers for advanced drug delivery systems, such as polyplex-releasing thermosensitive hydrogel systems for the controlled and local delivery of nucleic acids [3].

Figure 1. Schematic overview of polyplex formation using triblock copolymers (cationic block in yellow, uncharged hydrophilic block in blue and thermosensitive block in red).



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INVITED LECTURES

IL1

Crystallization, polymorphism, morphology and properties of olefin based di- and multi-block

Finizia Auriemma, Claudio De Rosa, Rocco Di Girolamo, Anna Malafronte, Miriam Scoti
Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Monte Sant'Angelo, via Cintia 21, 80126, Napoli, Italy
finizia.auriemma@unina.it

Abstract

The crystallization behavior, polymorphism, thermal and mechanical properties and thin film morphology of olefin-based di- and multi-block copolymers including crystallizable blocks are presented. The samples are obtained with use of non-metallocene single-site catalysts featuring living character for olefin polymerization, as it allows for preparation of block copolymers with precise control over the molecular mass, stereo- and regio-chemistry [1,2]. Recent results obtained in the study of crystallization and properties of di-block copolymers consisting of a polyethylene (PE) block covalently linked to a rubbery block of a random ethylene/propylene copolymer (EPR) (PE-EPR) [3], to an isotactic (iPP) and to a syndiotactic polypropylene [4,5] block (PE-iPP, PE-sPP, respectively). The mechanical properties and phase transitions occurring by effect of stretching are illustrated and the role of blocks length and chemical nature of accompanying block on polymorphism of PE, sPP and iPP is elucidated. The morphology which develops in thin films by effect of preparation conditions and/or by epitaxy onto specific substrates is shown, demonstrating the potential of epitaxy to obtain large-sized microstructures with well-oriented lamellar domains and long-range order, useful to template nanoparticle alignment [3-5] for fabrication of lithography masks, and for other relevant technological applications. In the second part, we illustrate the studies performed on some ethylene/1-octene multi block copolymers (EOBC) obtained from chain shuttling technology (CST) [2]. The chain shuttling polymerization was discovered by the DOW Chemical Company as an efficient tool to produce olefin multi-block copolymers in a single step, according to an economically favorable and continuous polymerization process [6,7]. The process is based on the use in the same reactor of two organometallic catalysts with different monomer selectivity, and diethyl zinc as chain transfer agent (CSA), for the reversible transfer of growing chains between couples of catalytic centers. The resultant products (EOBCs) are thermoplastic elastomers characterized by alternating crystallizable hard and amorphous blocks, with low and high octene concentration, respectively, and a statistical distribution in the block number and length/chain. We show that the crystallization properties of EOBCs and the structural organization of the chains which develops by effect of crystallization are strongly influenced by the statistical multiblock architecture, the tendency of the hard blocks to crystallize in separated domains, the short and polydisperse length of the hard blocks and the steric constrains imposed by the covalent bonding between the hard and soft blocks.

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IL2

Synthesis of aliphatic polycarbonates from carbon dioxide and epoxides promoted by [OSSO]-type transition metal complexes

Carmine Capacchione,[a] Veronica Paradiso,[a] Francesco Della Monica,[a] Stefano Milione,[a] Alfonso Grassi,[a] Luigi Cavallo[b]

[a] Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy

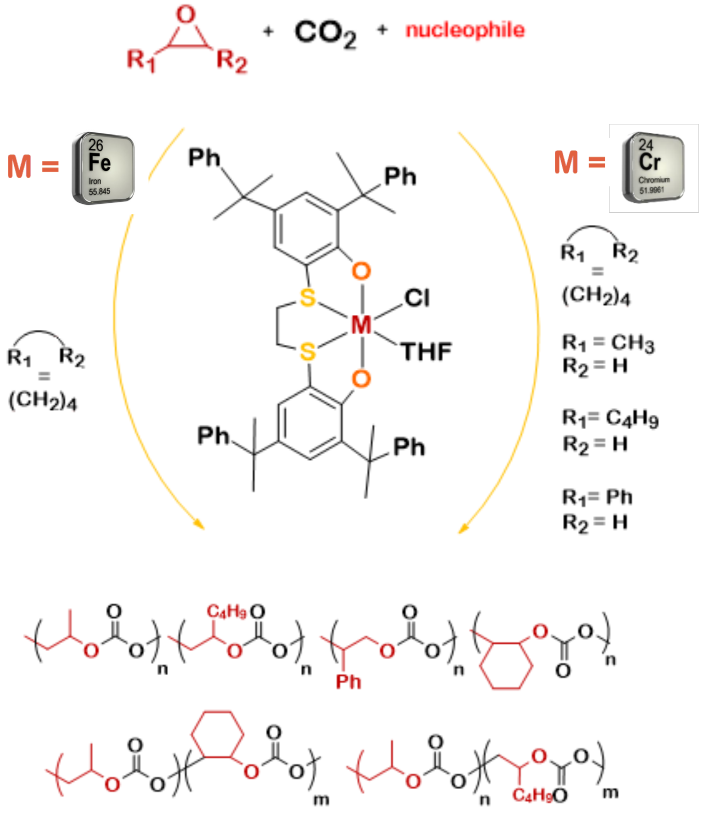
[b] King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

c.capacchione@unisa.it

Abstract

Copolymerization of CO_2 with epoxides represents a rising research topic, since it combines the utilization of this inexpensive, abundant, non-toxic gas with the production of biodegradable macromolecules, which is one of the major areas of development of the whole plastic field. Indeed, sustainable plastics are nowadays becoming a viable alternative to petroleum-based materials in a wide range of applications (including packaging, adhesives, elastomers) [1]. In the last years, many efforts have been devoted towards the exploration of various catalytic systems which are able to efficiently promote this transformation. Among them, one of the most studied is constituted by a transition metal (for example cobalt, iron and zinc) complex and a suitable nucleophile (commonly ammonium or phosphonium salts) [2,3]. In this context, the investigation of iron or chromium as the metal centre has been the subject of many studies, most of which regarding catalysts bearing nitrogen-donor ligands namely salan, salen or salalen [4]. A more recent advancement regards the utilization of sulphur-containing complexes and the resulting influence on copolymerizations of catalysts bearing this softer Lewis base [5,6]. In this contribution, we present an iron catalyst and a chromium catalyst bearing an OSSO-bisphenolate ligand, both suitable for the coupling of carbon dioxide and epoxides. By using propylene oxide, cyclohexene oxide, hexene oxide and styrene oxide and with a judicious tuning of the reaction conditions, polycarbonates were obtained with a high degree of selectivity (up to 100%).

Copolymerization of CO_2 with epoxides promoted by [OSSO]-type Fe and Cr complexes



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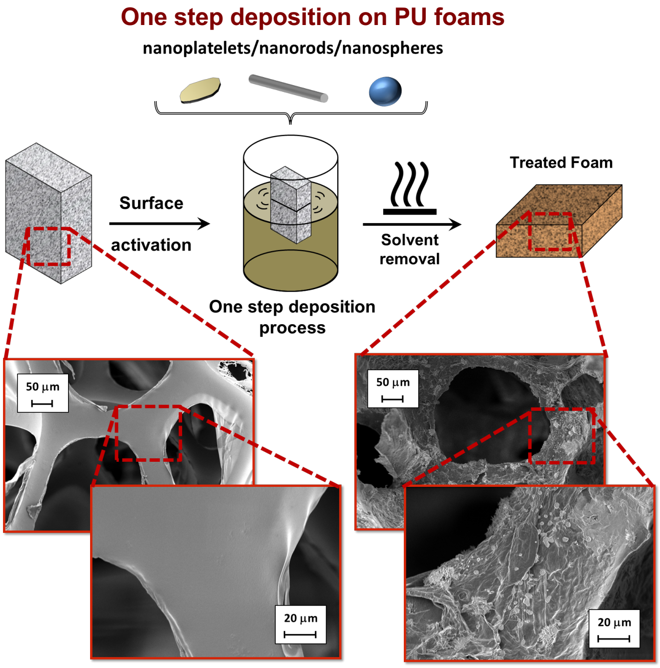
IL3

High performing flame retardant materials from surface nanostructuring of biobased components

Federico Carosio,[a] Lorenza Maddalena,[a] Julio Gomez,[b] Guido Saracco,[a] Alberto Fina[a]
[a] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria Campus, via Teresa Michel 5, 15121, Alessandria, Italy
[b] Avanzare Innovacion Tecnologica S.L, Avda. Lenticares 4-6. Poligono Industrial Lentiscares, 26370, Navarrete (la Rioja), Spain
federico.carosio@polito.it

Abstract

Polymer foams are widely used in many different applications in buildings, furniture and transport. In many of these applications, a controlled reaction to a flame exposure and a sufficient resistance to the flame are requested to guarantee safety in event of fire. Recent trends in materials science have clearly pointed towards the production of green and environmentally friendly material concepts capable of improving sustainability while also delivering optimized and competitive performances. Water-based surface deposition techniques such as the layer-by-layer assembly (LbL) have been proven to be effective in conferring flame retardant (FR) properties to polymer foams. [1,2] Treated foams usually achieve considerably reduced combustion rates and, in some cases, the ability to stop flame spread during flammability tests. [3,4] Self-extinguishing typically requires a high number of deposition steps (usually >10), which is currently preventing the scale-up and large scale industrial exploitation of the LbL approach. In the present contribution, we report the development of an efficient flame retardant approach capable of depositing nanostructured coatings on the surface of polyurethane foams (PU) characterized by with LbL-like structure and high FR performances by a single step procedure. Different kinds of nanoparticles (graphene nanoplatelets, montmorillonite clay, silica nanoparticles, sepiolite nanorods) have been selected and combined with natural polyelectrolytes (e.g. alginates) in order to deposit nanoparticle-filled polyelectrolyte coatings. The process deposits a homogeneous protective exoskeleton that completely wraps the 3D structure of the foam without altering its open-cell nature. The treated foams were capable of stopping flame propagation and completely suppressing the melt-dripping phenomenon during flammability tests in horizontal configuration. By cone calorimetry, all formulations were found able to considerably reduce the peak of heat release rate (pkHRR) by more than 65%. Smoke production was also efficiently limited, as demonstrated by total smoke release (TSR) reductions up to 75%. In addition, some of the most performing treated foams have been found able to withstand an impinging flame (temperature on the exposed side close to 800°C) and to maintain an excellent thermal insulation through the thickness. Indeed, the deposited protective exoskeleton the treated foams maintained structural integrity and successfully insulated the unexposed side with gradients greater than 500°C/cm comparable in performance to a commercial silica aerogel. Durability tests demonstrates that the treated foams maintain the achieved FR properties after being subjected to 1000 compression cycles. In summary, thanks to an efficient coating composition and by relying on a simple water-based approach it is possible to greatly improve the fire safety of flexible foams in several applications including upholstered furniture and seats for households, transports, public buildings, theatres/cinemas etc.).



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IL4

Microplastics in the environment: underestimated or overemphasized problem?

Valter Castelvetro, Andrea Corti, Virginia Vinciguerra, Alessio Ceccarini, Tommaso Lomonaco, Francesca Modugno, Jacopo La Nasa

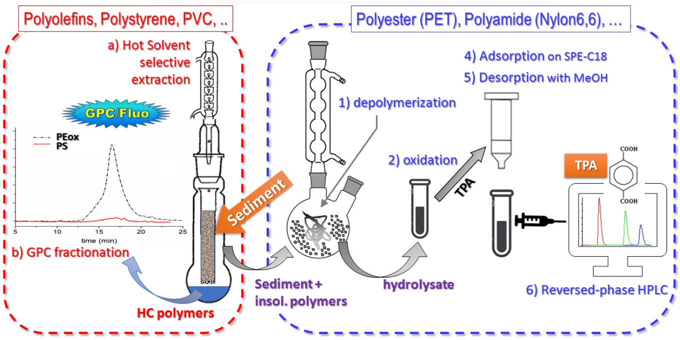
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi 13, 56124, Pisa, Italy

valter.castelvetro@unipi.it

Abstract

The presence of increasing amounts of micro- (MPs) and nano-plastics (NPs), including both primary (i.e. microfibers) and secondary (resulting from fragmentation of larger items) particles smaller than a few mm and down to the sub-micrometer range, represents a deceptive and multifaceted form of pollution. In fact, in addition to their still unclear role as harmful materials once internalized by animal species, they may act as: i) passive concentrators of toxic environmental pollutants (PAHs, halogenated aromatics, pesticides, etc.); ii) carriers of alien microbial populations; iii) active sources of harmful (e.g. as endocrine disruptors) or toxic leachate and volatile organic compounds (VOCs) resulting from the release of plastic additives and from polymer weathering. The main concerns with MPs and NPs is related to their still nearly unknown potential as directly or indirectly harmful species, and the lack of viable and effective solutions for pollution prevention and remediation. However, the first difficulty is their detection and quantification from a variety of environmental (natural waters, sediments, biota, soil) and man-produced (food products, wastewaters, etc.) matrices. The investigations reported so far have mainly dealt with particle isolation, counting and sporadic identification of polymer type; these methods are time consuming, inaccurate for statistically reliable environmental monitoring, and inadequate for the smallest sized particles hardly detectable by optical microscopy or micro-spectroscopy. Our approach was to design simple, robust, accurate and sensitive analytical procedures for the quantification of the concentration of the most common polymer types of MPs and NPs, that is, polyolefins (LDPE, HDPE and PP) and polystyrene (PS) resulting from the degradation of packaging material, as well as PET and polyamides that are mostly found as textile microfibers initially released in domestic wastewaters. Different strategies were adopted for the purification from matrices ranging from mainly inorganic (e.g. marine sediments) to mainly organic (e.g. fishmeal), and for the subsequent separation and quantification of the different polymers. The general procedure involves sample sieving at <2mm, followed by sequential extractions with hot solvents to remove soluble biogenic material and isolate PS and polyolefins [1,2]; then the residue is sequentially treated with strong acid and strong alkaline solutions resulting in selective hydrolytic depolymerization of polyamides and PET, respectively. Suitable purification of the different extract allows quantification of monomers or their derivatives by chromatographic (HPLC, GPC), hyphenated (Pyr-GC/MS) and spectroscopic (NMR, micro-ATR) analyticalc techniques [3,4] (see figure).

General analytical protocol for microplastics in sediments



Finally, the amount and type of degradation products released as VOCs from reference micronized polymers artificially aged in Solar Box and plastic debris collected from a marine beach were determined upon mild heating (60 °C) followed by headspace coupled to needle trap microextraction and GC/MS detection [5]. The results highlighted an increase of total VOCs along with the aging time, the VOCs composition and release rate as well as the extractable low MW fraction in polar solvents being strongly dependent on the type of polymer. In particular, polyolefins, PS and PET release significant amounts of harmful compounds, supporting the initial hypothesis that MPs represent an unrecognized source of pollutants potentially harmful for biota and human health.

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IL5

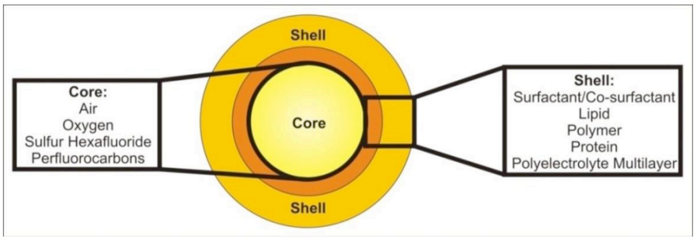
Polymer-shelled nanobubbles

Roberta Cavalli
Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, via P. Giuria 9, 10125, Torino, Italy
roberta.cavalli@unito.it

Abstract

Nanobubbles (NBs) are nanometer size bubbles. They were designed to obtain more efficient drug delivery systems. Indeed, their small sizes allow extravasation from blood vessels into surrounding tissues and ultrasound-targeted site-specific release with minimal invasiveness. Additionally, nanobubbles might be endowed with improved stability and longer residence time in systemic circulation [1]. NBs are constituted by three main parts: core, shell, and interface (surfactant layer). Core is made by a hydrophobic gas or vaporizable substances like perfluorocarbons (PFCs), sulphur hexafluoride, or a mixture of gases (Oxygen and PFCs) [2]. Shell is the barrier between the gas and the external environment. It can be made by lipids (i.e. phospholipids, cholesterol), proteins (i.e. albumin) or polymers (i.e. polysaccharides, PLGA, etc) [1]. Polymer-shelled nanobubbles have been designed to increase the stability and drug loading capability. The NBs polymer shell avoid gas dissipation from the interior to the exterior. In addition, targeting ligands can be conjugated to the polymer for specific site delivery.

Schematic representation of nanobubble structure



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IL6

Chemistry innovations that will change the world – Reversible Deactivation Radical Polymerization

Paweł Chmielarz

Department of Physical Chemistry, Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

p_chmiel@prz.edu.pl

Abstract

Atom transfer radical polymerization (ATRP) – one of the most versatile reversible-deactivation radical polymerization (RDRP) procedures [1] – has a few essential features, including narrow molecular weight distribution (MWD, M_w/M_n, *Đ*) and control over molecular weight (MW) of prepared macromolecules, and also the possibility to site-specific incorporation of functionalities [2]. Originally, traditional ATRP systems required high catalyst concentration (1,000–10,000 ppm) to maintain the activity during the polymerization [3]. Significant progress has been recently achieved allowing to diminish the concentration of Cu-based catalysts to the parts per million (ppm) due to an application of additional activator regeneration redox step. It can be triggered by introduction of a reducing compound *e.g.* radical initiator in initiators for continuous activator regeneration (ICAR) ATRP [4], chemical reducing agents (*e.g.* glucose [4], ascorbic acid [5], hydrazine[6]) and metallic silver [7, 8] in activators regenerated by electron transfer (ARGET) ATRP, zerovalent metals (Fe^0, Cu^0) [9] in supplemental activator and reducing agent (SARA) ATRP. Alternatively, an external stimuli such as a reducing current in electrochemically mediated ATRP (*e*ATRP) [10] and simplified electrochemically mediated ATRP (*se*ATRP) [11, 12], light in photo-induced ATRP (photo-ATRP) [13], or mechanical forces in mechanically induced ATRP (mechano-ATRP) [14] and in ultrasonication-induced ATRP (sono-ATRP) can be applied [15]. Electrochemistry offers additional opportunity to catalyst recycle [16], eliminates needs for chemical reducing agents , provides temporal control during the process [17], and extends polymerization to aqueous media [18]. Sono-ATRP eliminates a necessity of using an additional chemical compound as a reducing agent and in the context of environmentally friendly approaches which apply external stimuli – enables control of the polymerization rate by switching ultrasonication on/off, but uses a simple and easy to scale-up reaction setup, while resulting in excellent control during polymerization receiving macromolecules with high MW and narrow MWD [15]. Additional eco-friendly aspect in ATRP is replacing organic by heterogeneous media characterized by low toxicity, low viscosity and also good heat transfer taking advantage in industrial application, especially in the context of biomedical and pharmaceutical application [19]. Environmentally friendly aqueous and miniemulsion systems provide better thermal control and higher rate of polymerization. The main objective of this study is to present recent advances in RDRP in relation to the synthesis of well-defined materials with different architecture and composition, such as consisting of the hydrophilic core and the amphiphilic arms. The general concept of this method will be overviewed, followed by discussion of mechanism, apparatus, advantages and limitations.

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Acknowledgments

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IL7

Microplastics released from textiles: impact and mitigation strategies

Mariacristina Cocca, Francesca De Falco, Emilia Di Pace, Roberto Avolio, Maria Emanuela Errico, Gennaro Gentile, Maurizio Avella

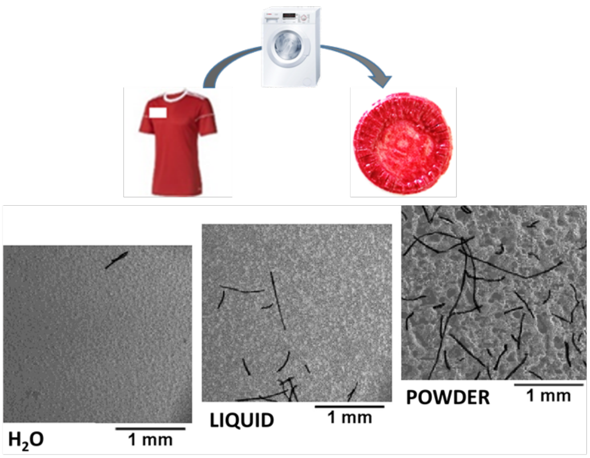
Institute for Polymers, Composites and Biomaterials CNR, via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy

mariacristina.cocca@ipcb.cnr.it

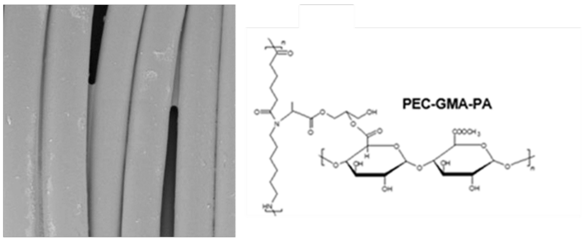
Abstract

During the last five years, research activities have been focused on the study of structure-properties relationship of synthetic fabrics to determine the main factors that affect microplastic release. Nowadays, microplastics released from synthetic fabrics are considered emerging pollutants with a wide distribution in the environment. These enter the environment as primary microplastics, generated during the washing process, in the wastewater and, generated by fabric abrasion, in the atmospheric fallout. Several analytical procedures have been set up to evaluate the extent of microfibres released from textiles during washings at lab scale [1], during laundering at real scale [2,3], and finally during textile wearing. Their application has allowed the determination of the effective contribution of the washing process to microplastic pollution as well as the identification of specific trends in microplastic release as a function of textile nature, structure and geometry, laundering detergents and additives, washing conditions and parameters. In order to reduce the impact of microplastics released from textiles, several mitigation strategies have been designed, by approaching this problem at its sources such as the fabric surface and the washing machine. In this respect, new finishing treatments were developed, based on the usage of natural and biodegradable polymers. The formation of a uniform and thin coating layer on fabric surface was proved to be effective in reducing more than 80% the amount of microfibres released during washing tests [4,5]. In addition, new filtration systems for laundry machine were designed and their effectiveness in reducing the amount of microfibres in wastewater was demonstrated.

Microplastic release from textiles



Effect of washing liquor



Mitigation strategies by innovative surface treatments

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IL8

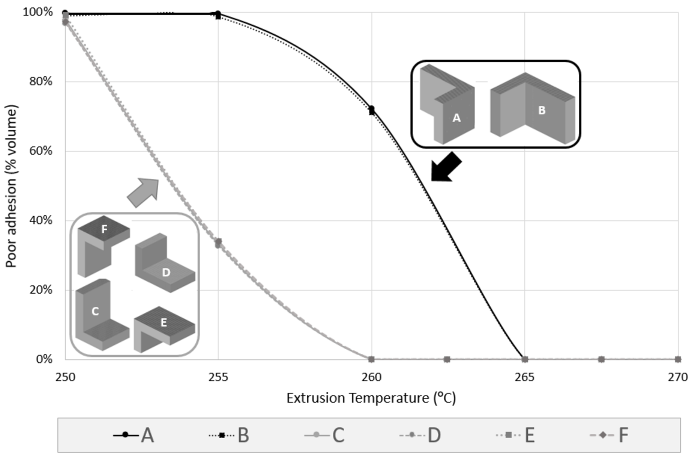
The cooling stage in extrusion-based 3D printing techniques

José Antonio Covas,[a] Sónia F. Costa,[b] Fernando Moura Duarte[a]
[a] IPC, Department of Polymer Engineering, University of Minho, Guimarães, Portugal
[b] CIICESI, Porto Polytechnic Institute (IPP), Felgueiras, Portugal
jcovas@dep.uminho.pt

Abstract

Additive Manufacturing (AM) techniques create 3D parts by adding successively 2D cross-sections in the vertical direction. In Fused Deposition Modelling (FDM) or Free Form Extrusion (FFE), each 2D cross-section is made by extruding and laying appropriately a molten filament. Despite of the well-recognized potential of these techniques, often the manufactured parts lack dimensional accuracy, surface quality and mechanical performance. These attributes are set during the deposition stage and depend strongly on the adhesion between contiguous filaments, which, in turn, are determined by the local filament temperature. The authors developed a code to predict the evolution of temperature and of adhesion of a filament during deposition and until cooling is completed [1,2]. It contains an analytical solution to the transient heat conduction process that is coupled to an algorithm that activates the relevant boundary conditions for each specific deposition sequence and to a procedure to compute the adhesion quality between adjacent filament segments. Input parameters include the material properties, the geometry of the part and the main process parameters, such as extrusion velocity, sequence of deposition and environment temperature. The predictions were experimentally validated. In this work, the code is used to study the effect of the main operating parameters on the evolution of cooling and on the resulting adhesion quality for a number of representative case studies.

Influence of extrusion temperature on the adhesion of a part manufactured with different build strategies



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IL9

The amazing world of network polymers and their applications

Dagmar R. D'hooge,[a,b] Lies De Keer,[a] Eva Loccufier,[b] Kilic Karsu,[c] Paul H. M. Van Steenberge,[c] A. Kislyak,[a,d] Hendrik Frisch,[d] Lode Daelemans,[b] Klaartje De Buysser,[e] Marie-Francoise Reyniers,[a] Christopher Barner-Kowollik,[d,f] R. W. Dauskardt[b], Karen De Clerck[b]

[a] Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, 9052 Ghent, Belgium
[b] Centre for Textiles Science and Engineering (CTSE), Ghent University, Technologiepark 70a, 9052 Ghent, Belgium
[c] Department of Materials Sci. and Eng., Stanford University, 416 Escondido Mall, Stanford, CA 94305-2205, USA
[d] School of Chemistry, Physics and Mech. Eng., QUT, 2 George Street, Brisbane QLD, 4000, Australia
[e] SCRiPTS, Department of Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S3, 9000 Ghent, Belgium
[f] Institut für Technische Chemie and Polymerchemie, KIT, Engesserstrasse 18, 76128, Karlsruhe, Germany
dagmar.dhooge@ugent.be

Abstract

Network materials are important both in nature and in the field of synthetic chemistry. Depending on the chemistry selected the degree or order of the molecular build-up of the network is altering, affecting the macroscopic properties. In the present work, a generic framework is presented that enables an unprecedented quantification of polymer network synthesis at the molecular scale, with as core matrix-based kinetic Monte simulations.[1,2] The framework enables to obtain at any synthesis time the 3D molecular structure of the network and hard to access molecular descriptors such as the molecular pore size distribution. The framework is illustrated for both inorganic and organic chemistry and is utilized to construct fundamental structure property relationships for several application fields, including curing, separation and drug delivery.

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IL10

Microplastics in deep water: a combined GC-MS e FT-IR approach

Enrico Davoli,[a] Giancarlo Bianchi,[a] Stefano Magni,[b] Andrea Binelli,[b] Luigi Falciola[c]

[a] Dipartimento Ambiente e Salute, Istituto di Ricerche Farmacologiche Mario Negri IRCCS, via Mario Negri 2, 20156, Milano, Italy

[b] Dipartimento di Bioscienze, Università degli Studi di Milano, via G. Celoria 26, 20133, Milano, Italy

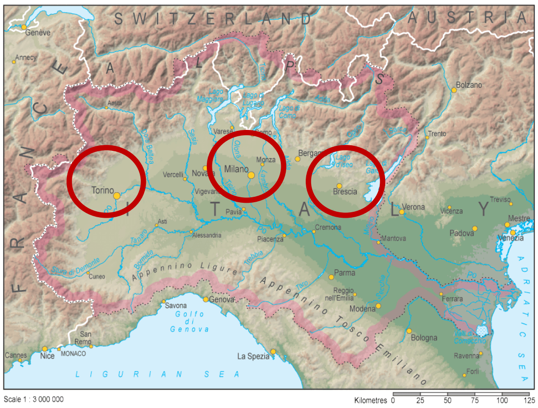
[c] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy

enrico.davoli@marionegri.it

Abstract

Microplastics are water-insoluble, solid polymer particles that are 1 to < 1000 μm in size [1]. A lower size boundary has not been defined, but particles below 1 μm are usually referred to as nanoplastics rather than microplastics. The ubiquity of microplastics [2] of all sizes in surface water, groundwater and wastewater has raised the question if pollution of drinking water occurs and to date, few studies indeed described the presence of this new contaminant in tap and bottled water [3]. Toxicity it is not yet well known [4], they might cause local inflammations in the gut, and a transport into organs might occur. As a final problem in this field, microplastics in the environment are difficult to sample, to identify and standardized methods do not exist. For this reason, we have been involved in a research project finalized to the definition of a protocol strategy for sampling and analysis of microplastics in drinking waters, coming from deep water wells, in the networks of three large cities in the Northern part of Italy. The project is on going and presently three groups of deep-water samples have been collected in the city of Milano, and in the Provinces of Brescia and Torino, before and after the treatment stages used for the urban network. Great attention has been paid to sampling and extraction steps as microplastic contamination, in this kind of samples, is expected to be very low [5] and contamination during sampling might occur through air or materials. Analytical methods have been defined for the detection of main microplastic contamination, like PE/PP, PS, PA, PVC and PET residues > 1 μm. Samples have been analysed first by a non-destructive approach using a Spotlight 200i microscope equipped with two different μATR probes coupled to an FT-IR spectrophotometer, followed by a mass spectrometric characterization of the polymers by a solid phase microextraction (SPME) GC-MS of thermal decomposition products (TED) of microplastic residues. Results will be presented and critically discussed.

Sampling sites for deep waters



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IL11

Plastics and polymers in Italian aquatic environments. Survey, monitoring, laboratory analysis and educational aspects

Luca Fambri, Denis Lorenzi, Roberto Caria, Riccardo Ceccato, Giada Bombardelli, Claudia Gavazza, Alfredo Casagranda
Dipartimento di Ingegneria Industriale, Università degli Studi di Trento, via Sommarive 9, 38123, Trento, Italy
luca.fambri@unitn.it

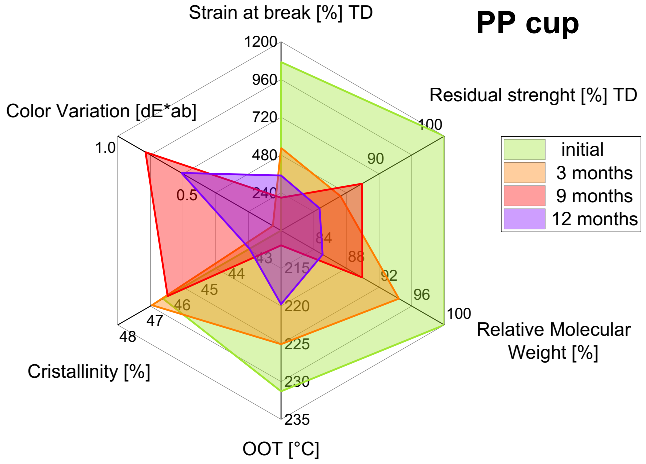
Abstract

The plastic contamination in aquatic environment, both marine and lake shoreline, will be presented. The formation of secondary microplastics is caused by the fragmentation of larger items due to a combined effect of various factors. Micro-mechanical stresses, air and water and sun-light exposure determine not only a progressive cracking of physical integrity, but also a chemical modification of the polymer chains. Various plastics debris and specific plastic items have been characterized by chemical-physical properties [1], and the results of three set of data will be compared.

1) Marine Plastics Survey. Selection of plastic wastes was collected from various beaches and shore-lines of Tyrrhenian Sea, Ioniam Sea and Adriatic Sea, as precursor of microplastics in the Mediterranean Sea [2].
2) Controlled Plastics Degradation in Marine Zones. The progressive decay of physico-chemical properties of some common polymers (PS, PE, PP, PET, PLA) was evaluated following the evolution of properties after 3, 6, 9 and 12 months of exposition to natural aging conditions in marine environment at Villasimius (CA), Italy. Plastic cups, bottles, foams and films were positioned i) in the beach sandy shoreline, and ii) in seawater at various depth. Figure 1 shows the decay of PP properties.
3) Lake Plastics Survey. The exceptional meteorological event (Vaia 2018, gales of up to 120 km/h) provided the opportunity to evaluate the level of plastic wastes diffusion in the local sub-alpine region (Sarca basin, Adige zone, Garda lake). Several macroplastics and microplastics were collected with also the contribute of the local students from Liceo Maffei (Project Tirocinio Formativo–Curriculare AS 2018/19) even after 4, 8 and 12 months. In selected positions of 1-2m2 (identified by gps) the collected samples were identified and classified (by number, weight, average weight).

Various lab techniques were performed in order to i) identify the type of plastic (FTIR) and to ii) determine the grade of physico-chemical degradation of film, cups, bottles, foams, fragments et al. Thermogravimetry (TGA) and calorimetry (DSC) showed a specific dependence on physical-chemical aging. In particular thermal stability, oxidative degradation, glass transition temperature, melting and crystallization behaviour of semicrystalline polymers (PE, PP, PET, PLA) were compared to the correspondent virgin polymers. Oxidation Onset Temperature (OOT) for PE, PP and PS specimens was considered as a preliminary index of oxidation/degradation. Tensile tests were performed on specimens taken from longitudinal and/or transversal direction (film, cups, bottles). Moreover, different rheological tests were used to evaluate the molecular weight (capillary viscometry for PLA and PS; rotational melt viscometry for polyolefins). Colorimetry tests were performed to evaluate the yellowing, due to macromolecules' oxidation. Specific observations and lab-level characterization of various aged plastic objects gave interesting information of the aging effect. Geometrical size (thickness) has been evaluated as key-factor for formation of polyolefin microplastics, as function of aging time. Mechanical properties were compared with those of correspondent new products, and their relative variation could be considered as a weathering index. A promising result is also the activity of dissemination and active recruitment of high school students for the evaluation of microplastics contamination.

Figure 1. Example of properties' decay of PP cup after 3, 9 and12 month of ageing in sea-water (Villasimius, CA)



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IL12

Mimicking microplastic pollution through more realistic reference materials

Stefania Federici,[a,b] Serena Ducoli,[a,b,c] Claudio Marchesi,[a,b] Monika Rani,[a,b] Elza Bontempi,[a,b] Laura E. Depero[a,b]

[a] Dipartimento di Ingegneria Meccanica e Industriale, Università degli Studi di Brescia, via Branze 38, 25123, Brescia, Italy

[b] INSTM, via Giusti 9, 50121, Firenze, Italy

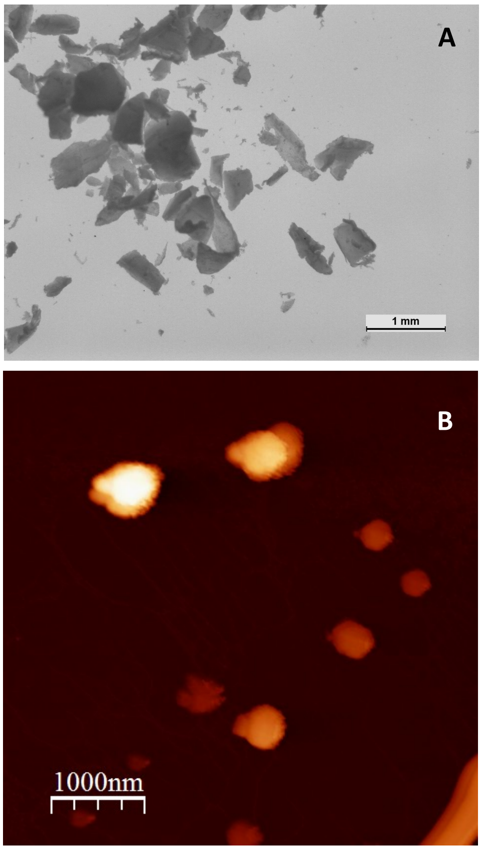
[c] Dipartimento di Ingegneria dell'Informazione, Università degli Studi di Brescia, via Branze 38, 25123, Brescia, Italy

stefania.federici@unibs.it

Abstract

Plastics entering in the environment represent a global and recognized issue for wildlife and humans. However, beyond the visible macroscopic pollution, there is a silent degradation process that leads to the breakdown of the bigger pieces of plastic litter into smaller, and potential dangerous, fragments that reach the micro- and nanoscale [1]. The limitation in size of these particles negatively affects the development of adequate methods for qualitative and quantitative studies [2]. The lack in the methodological pathway is also hampered by a strong need to create good reference materials in order to perform more representative studies of the interaction between plastic particles and the environment or organisms. Small plastic fragments are far for being modelled by ideal particles commercially distributed for laboratory studies. The reason is that this kind of sub-micrometer particles cannot be considered as virgin materials synthesized with the desired size, shape, surface, and composition. Indeed, the weathered particles are polydispersed, they could reach random shapes, and heterogeneous surface chemistry, that could drive unexpected results if compared to the pristine ones. In this contribution, the preparation of more realistic reference materials to study micro and nanoplastics will be presented. Starting from daily used disposable plastic items, different techniques to fragment or degrade macro-pieces in a controlled way, such as mechanical disruption or photodegradation, are employed. For fragments at the nanoscale, methods to preconcentrate and to separate particles into specific size fractions are also applied. For fragments at the microscale, chemometric tools are used to build up predictive models for unknown concentrations of microplastic mixtures. Finally, the presented approach combines consolidated techniques in the field of nanomaterials analysis, such as imaging techniques, size distribution and physical-chemical characterization techniques, as vibrational spectroscopy, to characterize the produced micro- and nanoplastic samples, posing particular attention to the innovative portable measuring instruments.

Reference material for micro and nanoplastics



(A) Optical microscope image of microplastics. (B) AFM image of nanoplastics.

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IL13

Injectable nanocomposite hydrogels for controlled cell migration and local drug delivery applications

Nermin Seda Kehr

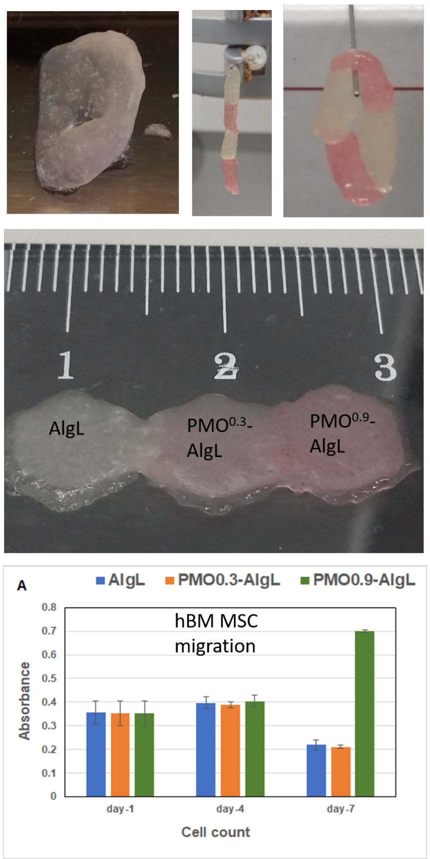
Physikalisches Institute and Center for Soft Nanoscience, Westfälische Wilhelms-Universität Münster, Busse-Peus-Strasse 10, 48149 Münster, Germany

seda@uni-muenster.de

Abstract

One of the basic goals of biotechnology is to create engineered biomaterials to mimic natural extracellular matrix characteristics to be able to study and/or control cell-biomaterial interactions. Recent interest has focused on the fabrication of biomaterials using 3D printing technique. Although, 3D printing offers good control on the spatial arrangement of components with different biophysicochemical features in the 3D network of complex architectures, there are few studies use this technique to generate multifunctional materials. Therefore, in this context, we described Injectable Step-Gradient Nanocomposite (NC) hydrogels as new multifunctional constructs [1,2]. These multifunctional biomaterials were generated using 3D printing technique and design to study and compare simultaneously the effect of different (bio)chemical and physical parameters on cell behaviour (e.g., hBM MSC adhesion, migration, differentiation). Step-gradient NC scaffolds were created by 3D printing of various polymer pastes loaded with different concentration of nanoparticles. The respective cell experiments demonstrated biomolecule and nanoparticle concentration dependent cell adhesion and migration in the 3D step-gradient NC scaffolds [1]. We propose that our approach of preparing multifunctional constructs by connecting various polymer/nanoparticle composites with different (bio)chemical and physical properties with the help of 3D printing technique can be easily adapted to generate other advanced systems for different applications, in particular in the biomedical fields of wound healing, local drug delivery [3], and tissue engineering.

Injectable NC Hydrogels for hBM MSC migration



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Acknowledgments

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IL14

On the key role of carbonaceous filler distribution for advanced polymer-nanocomposites

Marino Lavorgna,[a,b] Giovanna G. Buonocore,[b] Gennaro Rollo,[a] Chiara Santillo,[b] Yanhu Zhan,[c] Hesheng Xia[b,d]

[a] Institute for Polymers, Composites and Biomaterials, via Previati 1/E, 23900, Lecco, Italy

[b] Institute of Polymers, Composites and Biomaterials-CNR, piazzale Fermi 1, 80055, Portici (NA), Italy

[c] School of Materials Science and Engineering, Liaocheng University, Liaocheng, China

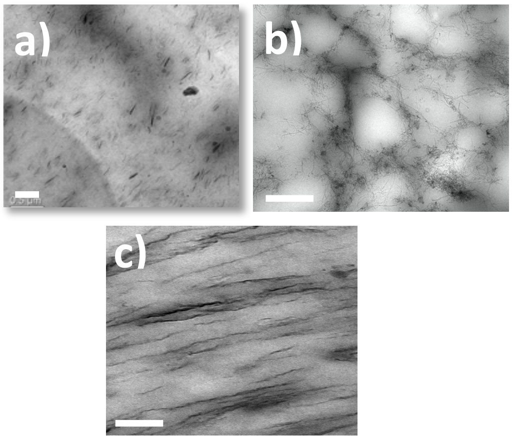
[d] State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, China

marino.lavorgna@cnr.it

Abstract

The properties of carbonaceous filler (i.e. graphene and its derivatives and carbon nanotubes)-based polymer composites depend on the interfacial interactions between the filler and the polymeric matrix as well as on the spatial localization of filler particles, being possible different morphologies: homogeneous random dispersion, 2D-layered distribution, 3D-filler network (commonly indicated as "segregated morphology"). In the last years, several research activities have been mainly focusing on the exploitation of innovative approaches for tailoring the spatial distribution of fillers within the polymeric matrix in order to enhance both functional and structural properties, with an understanding focus on correlating morphology, processing and properties. The resulting composites, realized as films, coatings and aerogels and foams, often represent an effective solution to face specific societal challenges of transport, buildings, cultural heritage, environment protection, health application sectors. In this scenario, this work is addressed to correlate the experimental approaches to tailoring the final filler-morphology and the multifunctional properties of the resulting composites. As example, here it is overviewed the results obtained from the following activities: A) Latex mixing and co-coagulation process for the preparation of rubber/filler composites with a reduced Graphene Oxide (rGO) and Carbon Nanotubes "segregated" network, realized as bulk elastomer, layered and porous materials, with enhanced mechanical, electrical and EMI shielding properties. The results highlight the importance of the "segregated morphology", as compared with the random distribution of the filler, in reducing the needed filler amount to get the electrical percolation. Consequently, the "segregated morphology" also enhanced significantly other functional properties, such as barrier property, mechanical and thermos-mechanical properties of the rubber-based composites. B) Unidirectional or Bi-directional freeze-casting approach for the realization of complex structures (i.e. natural rubber composites and open-cell polyurethane foam filled with rGO/chitosan aerogel) with anisotropic electrical conductivity and piezoresistive properties. The results highlight that the resulting porous materials have excellent sensing properties being able to detect changes in solvents, temperatures, and compression stimuli.

Figure 1. Spatial distributions of carbonaceous fillers in polymers: a) random morphology of graphene in rubber; b) "segregated morphology" of CNTs in rubber and c) layered morphology of graphene nanoplatelets in chitosan matrix (the white bar is 500 nm)



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IL15

Single Use Plastics directive: EU policies push plastic industry towards a responsible future

Mario Malinconico[a,b]

[a] Institute for Polymers, Composites and Biomaterials, Consiglio Nazionale delle Ricerche, via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy

[b] International Solid Waste Association, via del Poggio Laurentino 11, 00144, Roma

mario.malinconico@ipcb.it

Abstract

The European Parliament approved the disposable plastic directive in March 2019. It will probably be implemented within the member states by 2021. The rules concern the ten articles most frequently found on European beaches. The measures include a ban on disposable plastic products for which there are alternatives on the market - cotton buds, cutlery, plates, straws and mixers for drinks as well as glasses, containers for food and drinks made of polystyrene and on all products made of oxodegradable plastic, in addition to the sticks for balloons. The directive also provides for the objective of reaching 90% in the separate collection of plastic bottles by 2029 (77% by 2025) and the introduction of design requirements to connect the caps to the bottles as well as the objective of incorporating the 25% recycled plastic in PET bottles by 2025 and 30% in all plastic bottles by 2030. The Directive follows on from the "European strategy on plastic in a circular economy", published by the European Commission in early 2018. It contains plans to reduce waste, put an end to the dispersion of waste in the seas and make plastic recycling more profitable for companies in the European Union. By 2030 all plastic packaging on the EU market will have to be recyclable. The circular economy, an essential paradigm of sustainable development, has found a powerful allied in the bioeconomy, based on the principle of reducing dependency on non-renewable fossil fuels for all sectors of commodities. In this scenario, plastic is at the center of attention, both for the environmental implications of packaging, and for the real possibility, today, of developing the biorefinery chain on it. Research focuses on the development of chemical and chemical-physical technologies to facilitate the recovery and reuse of plastics. Another topic of great attention is the development of biodegradable and compostable plastics. The latter, without compromising the level of safety in the management of consumer goods, such as food products, today guaranteed by polyolefin-based plastics, can be managed at the end of life as organic matter and therefore can follow the supply chain compostable fraction of waste. The balance of these two options, recycling and biodegradability, can be the guarantee of a better future.

IL16

Publishing in a more interconnected and diverse world

Leanne Mullen
Materials Today team, Elsevier, The Boulevard, *Langford Lane*, Kidlington, Oxford OX5 1GB, UK
l.mullen@elsevier.com

Abstract

I completed my PhD in Materials Science from the University of Cambridge in 2010 and moved to publishing in 2012. I am currently Senior Publisher of *Progress in Polymer Science*, *Giant*, *Materials Today Bio, Materials Today Chemistry, Polymer*, *European Polymer Journal*, *Polymer Degradation and Stability*, *Reactive and Functional Polymers*, *Progress in Organic Coatings* and *Polymer Testing*. I also manage both the International Conference on Multifunctional, Hybrid and Nanomaterials and the International Symposium Frontiers in Polymer Science which are held every two years. In addition to publishing materials journals Elsevier also support several important community awards including the Materials Today Agents for Change awards and the Materials Today Rising Star Awards [1,2]. Elsevier also launched a mid-career Materials Today EPJ Award on *European Polymer journal* in 2018 and the window for new submissions for the 2020 award is now open [3]. It is estimated that 225,000 researchers join the research community each year, while 43% of PhD's graduate without having secured employment. In times of "publish or perish", it's also worth noting that between 30 and 50% of all research papers submitted to journals end up in the "desk reject" pile – where for a number of different reasons, ranging from being outside of the scope of a journal to language inadequacies, papers never even make it to the peer review stage. To address this, we give talks in different institutes and conferences around the world to support researchers to get published, to attract new referees, board members and editors. In 2018, Elsevier relaunched its free e-learning platform, formerly Publishing Campus, as Researcher Academy [4]. The e-learning modules and countless resources at Researcher Academy take you through the different phases of the research cycle – from the beginnings of research preparation, through the publishing process, all the way to demonstrating impact The focus of this talk is to introduce my journals and the extended family of Materials Today Journals and to share some tips on journal selection and getting published. I will also outline the increase in open science publishing, including our new Open Access titles and highlight the qualities and expertise we look for when appointing Board Members, Editors and Editors in Chief. We will also discuss the wider publishing landscape and share best practices and practical tips for publication in high impact journals such as *Materials Today* and Elsevier's Polymer family of journals, as well as new initiatives for increasing diversity and inclusion within our editorial boards and conference series.

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IL17

Microplastics identification via holographic imaging and machine learning

Melania Paturzo,[a] Vittorio Bianco,[a] Pasquale Memmolo,[a] Francesco Merola,[a] Pierluigi Carcagnì, [b] Cosimo Distante,[b] Pietro Ferraro[a]

[a] CNR-Institute of Applied Sciences & Intelligent Systems, via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy

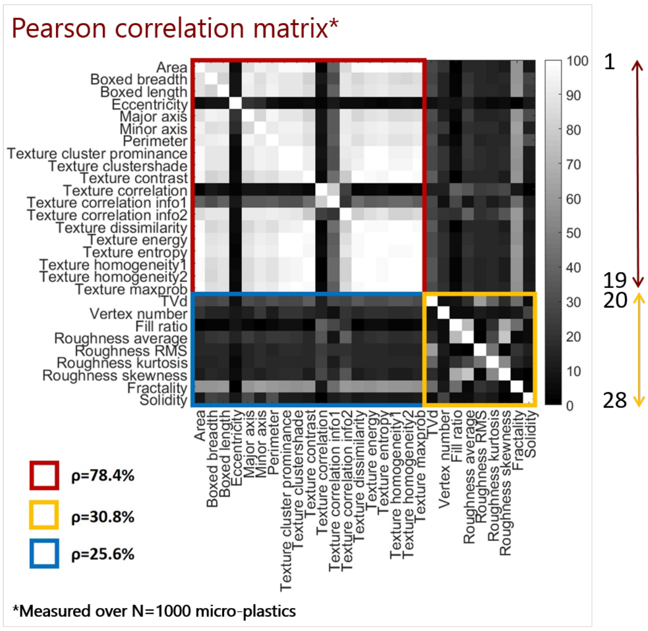
[b] CNR- Institute of Applied Sciences & Intelligent Systems, via Monteroni sn, 73100, Lecce, Italy

m.paturzo@isasi.cnr.it

Abstract

Microplastics are small plastic particles the size of less than 5 millimeters deriving from abrasion or progressive fragmentation of larger plastic items or being manufactured to be of a small size for use in cosmetics. The uptake of microplastics by living organisms may cause injuries of the gastrointestinal tract, trigger inflammation or cause cell toxicity by intrinsic particle properties or adsorbed pollutants. The tremendous marine pollution by plastic particles and fibers and their increasing presence in the human environment demands for effective detection methods. So far, analytical methods for identifying and counting MPs are still only at a basic developing stage. Typically, analytical procedures for MPs identification in environmental samples consist of multiple steps, i.e. extraction, isolation, identification, and classification. As long as the sizes of MPs stay in the range 1-5 mm, visual sorting by expert users has been adopted for detecting them. Hence, an automated and robust identification and counting method is highly demanded to perform the effective ecological risk assessment, especially at micrometer scales. Indeed, under 1 mm, the identification of each single object inside a pretreated water sample is usually made by unaided eyes at the optical microscope. Pretreatment steps usually include digestion, sieving or filtration of natural water in order to exclude sediments falling outside the analysis range and to avoid coating of microplastics by bacteria biofilm or marine algae. After their physical characterization by using optical microscopes, MPs are chemically characterized through spectroscopy methods for assessing the plastic type. This procedure is intrinsically low-throughput, time consuming and not deployable in situ for continuous and/or rapid monitoring. Therefore, a processing protocol for rapid and automatic MPs recognition is still missing. In this framework, investigating methods to reliably detect the presence of MP in a water sample is a highly pursued objective. Here, a new approach is presented that combines 3D coherent imaging with machine learning for achieving accurate and automatic detection of microplastics in filtered water samples [1]. The water pre-treatment process eliminates sediments and aggregates that fall out of the analysed range. However, it is still necessary to distinguish clearly microplastics from marine microalgae. Here we show that, by defining a novel set of distinctive "holographic features", it is possible to identify accurately microplastics within the defined analysis range. The process is specifically tailored for characterizing the microplastics "holographic signatures" thus boosting the classification performance and reaching accuracy higher than 99% in classifying thousands of items. The machine learning approach in conjunction with holographic coherent imaging is able to identify microplastics independently from their morphology, size, and different types of plastic material.

Pearson matrix corresponding to the MPs



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IL18

Fibrin as a cell matrix. Cell-mediated contraction and other phenomena

Nicola Tirelli[a,b]

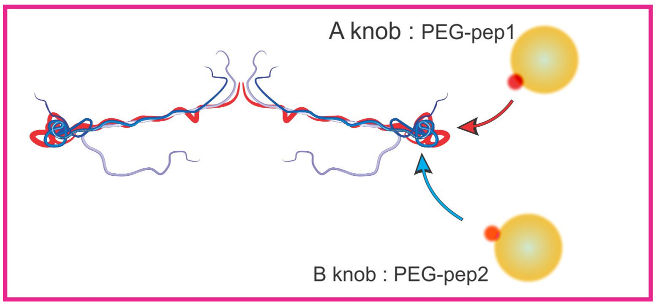
[a] Laboratory of Polymers and Biomaterials, Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy

[b] Division of Pharmacy and Optometry, University of Manchester, Oxford Road, M13 9PT, Manchester, United Kingdom

nicola.tirelli@iit.it

Abstract

Besides being the material at the basis of the blood coagulation, fibrin is also a biomaterial widely applied in the clinic as an haemostatic agent and as a tissue adhesive, and with a history of use in tissue engineering [1]. Recently, we have tackled two issues that have somehow hindered its broader use in regenerative medicine: its precise molecular engineering, and its cell-mediated contraction. In terms of molecular engineering, we have implemented an approach that employs the same affinity interactions leading to fibrin self-assembly and fibrillogenesis during blood clotting [2]; in this way, it is possible to introduce artificial components (e.g. PEG as in Scheme 1) with good topochemical control on to fibrinogen and then on to fibrin fibres. In the presentation, we will discuss how this tool can be used to control cell motility. For what attains to cell-mediated contraction, we have embarked in a quantitative characterization of how mesenchymal cells (in this case, mostly dermal fibroblasts) are capable to exert bulk or interfacial contraction onto fibrin matrices, as a function of fibrin modulus and of the presence of fibrotic (pro-contraction) factors. In the presentation, we will specifically discuss issues related to the alignment of both cells (Figure 1, left) and matrix components (Figure 1, right).



Scheme 1

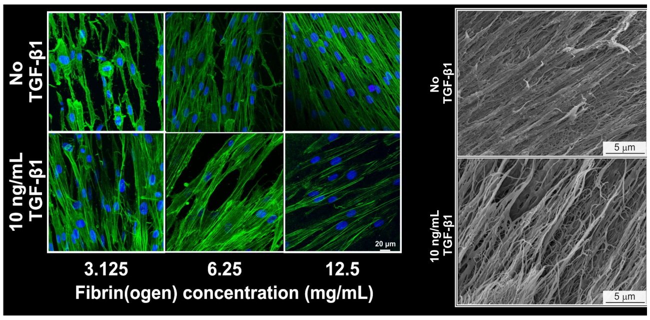


Figure 1

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ORAL COMMUNICATIONS

OC1

Highlights on the degradation of polyamidoamines in water and in soil

Matteo Arioli, Jenny Alongi, Amedea Manfredi, Paolo Ferruti, Elisabetta Ranucci
Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy
arioli.matteo95@gmail.com

Abstract

The persistency of plastic waste in the environment has made the development of degradable polymers a relevant issue. Polyamidoamines (PAAs) are a class of degradable and mostly biocompatible polymers deriving from the Michael-type polyaddition reaction of bis-acrylamides with amines. The reaction is normally carried out at room temperature in the absence of added catalysts [1]. The use of *prim*- or bis-*sec*-amines produces linear, in most cases water-soluble polymers, while the use of multifunctional amines with more than two mobile hydrogens provides crosslinked polymers giving hydrogels in the presence of water. A small library of linear PAAs with molecular weight in the range 7-20000 were prepared by combining three bisacrylamides, namely N,N'-methylene bis-acrylamide, 2,2-bis(acrylamido)acetic acid and N,N'-bis-acryloylpiperazine, with different amines, namely glycine (GLY), ethylamine ($EtNH_2$) and 2-methylpiperazine (2MeP). Hydrogels were also obtained from a reaction mixture containing 1:0.7:0.15, on a molar basis, bisacrylamide/amine/ethylenediamine. The degradation of the linear PAAs was first studied by monitoring the decrease in molecular weight on time at 25°C in pH 8.0 buffer solution by means of Size Exclusion Chromatography. In a second type of experiment, ^1H NMR spectroscopy was used for identifying the structural changes of PAAs during degradation in water. In order to study the pH dependence of the degradation, analyses were conducted in D_2O solution at pH 4, 7 and 9, respectively. The effect of temperature and concentration was also investigated. The results showed that the prevailing mechanism of degradation is the depolymerization reaction. The soil degradation of solid linear PAAs was also studied by monitoring the CO_2 produced as a consequence of biodegration by using a modified closed bioflask system according to the literature [2]. Degradation turned to be dependent on both the nature of the amine and the amide moieties present in the polymer repeating units. Glycine-based polymers showed the highest degradation rate in all tests, while 2MeP-based the lowest. As for hydrogels, the degradation behavior was studied in water by monitoring the variation of the apparent volume on time at 25°C until swelling complete disappearance of any insoluble matter. Preliminary toxicity tests according to the seed germination tests [3] were performed. Root elongation of *Lepidium sativum L.* germinating seeds after 3 days exposure was monitored in the presence of PAA aqueous solutions at different concentrations, using plane water and a 0,1% dichromate solution as positive and negative standards. It was observed that a polymer solution from 0.01 to 1 mg/mL did not exert any adverse effect on the root growth. On the opposite, the root growth was even higher than in plane water. At higher PAA concentrations, some toxicity effects were observed. In particular, at 1 to 10 mg/mL the growth was slower and at concentration higher than 10 mg/mL it was completely inhibited.

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OC2

Homo- and copolymeric polyamidoamines as flame retardants for cotton fabrics

Alessandro Beduini,[a] Federico Carosio,[b] Paolo Ferruti,[a] Elisabetta Ranucci,[a] Jenny Alongi[a]
[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy
[b] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria campus, viale T. Michel, 15121, Alessandria, Italy
alessandro.beduini@studenti.unimi.it

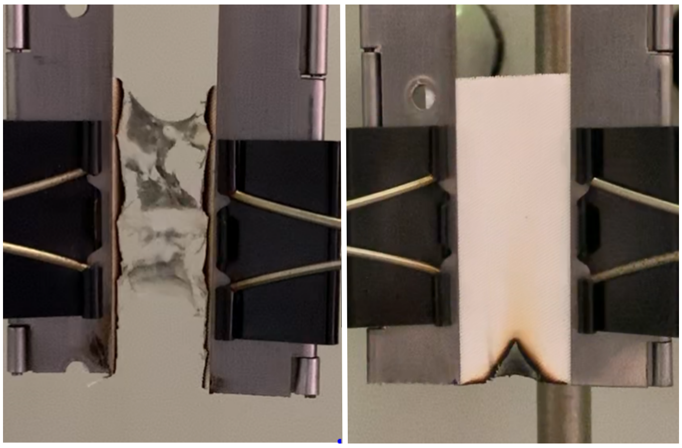
Abstract

Previous works have shown that a class of bio-inspired polymers named polyamidoamines (PAAs) have a potential as surface confined flame retardants for cotton. In particular, carboxylated-PAAs extinguished the flame in horizontal flame spread test (HFST) at 5% add-on due to their intrinsic intumescence [1], while disulphide-based polyamidoamines (SS-PAAs) were effective in both horizontal and vertical flame spread tests (VFST) at 16% add-ons thanks to their intrinsic intumescent features and radical scavenger activity [2]. Surprisingly, however, in HFST the efficacy of SS-PAAs was somewhat inferior to that of its sulphur deprived analogues. It was hypothesized that copolymers between a sulphur deprived and SS-PAAs could combine the merits of both as flame retardants [3]. Specifically, the copolymers were obtained by reacting glycine (G)/cystine (C) at different molar ratios with N,N′-methylene bisacrylamide (M). Polymerizations were carried out in water, at room temperature and with no added catalysts. The resulting copolymers (70:30, 60:40, 50:50 and 30:70 G:C molar ratio) were characterized by infrared spectroscopy in attenuated total reflectance configuration (FT-IR/ATR), and hydrogen nuclear magnetic resonance (^{1}HNMR). The treatment of cotton fabrics was carried out by the impregnation method., copolymer water solutions at pH 9. Strips of cotton fabrics were dried for 2 min at 90 °C and weighed. 7 wt.-% copolymer aqueous solutions were uniformly dropwise distributed on the specimens. After deposition, samples were dried 10 min at 100 °C. The total dry solid add-on (wt.-%) was determined by weighing each sample before (W_i) and after impregnating and drying (W_f). The add-on was calculated according to Equation (1):

$$\text{Add-on\%} = [(W_f - W_i)/W_i] \times 100 \qquad \text{Eq. 1}$$

The final add-on was approximately 16% for all samples. The performance of the M-G-C S-based copolymers was compared with those of the related M-G and M-C homopolymers and those of M-G/M-C blends of the same composition. Furthermore, samples coated with i) 50:50 blends of the M-G and M-C homopolymers; ii) two layers of M-G and M-C, respectively, (~ 8% add-on for each layer) were prepared. All samples were characterized by FT-IR/ATR, thermogravimetry (TGA), vertical flame spread tests (VFST) and horizontal flame spread tests (HFST). In previous work it was found that in VFST tests the M–C homopolymer inhibited cotton ignition at 16% add-on, whereas M–G failed to extinguish the flame even at 30% add-on. In the present investigation, the copolymers with C content > 50% performed as M–C. By contrast, all blends failed to extinguish the flame. In previous work the M–G homopolymer showed better performance than M–C in the HFST test, extinguishing the flame at add-ons of 5% and 12%, respectively. In this work, it was found that the M–G_{50}–C_{50} copolymer extinguished the flame at an add-on of 7%. It may be concluded that the M–G_{50}–C_{50} copolymer combines the merits of the related homopolymers both in VFST and HFST.

Comparison between untreated cotton and cotton treated with M-G_{50}-C_{50} after VFST



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Acknowledgments

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OC3

Deformable molecularly imprinted nanogels

Alessandra Maria Bossi,[a] Roberta Tatti,[a] Nunzio Cennamo,[b] Luigi Zeni[b]

[a] Dipartimento di Biotecnologie, Università di Verona, Strada Le Grazie 15, 37134, Verona, Italy

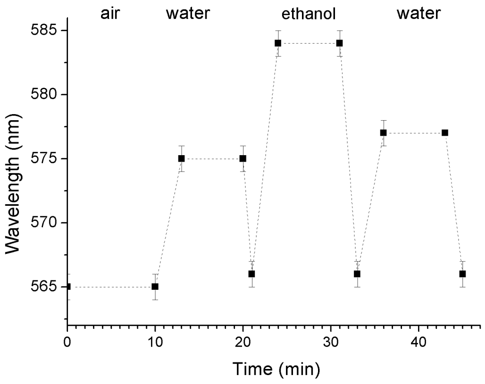
[b] Dipartimento di Ingegneria, Università Della Campania Luigi Vanvitelli, via Roma 29, 81031, Aversa (CE), Italy

alessandramaria.bossi@univr.it

Abstract

Polymer biomimetics prepared by the technique of molecular imprinting (MIPs), i.e. a template assisted synthesis [1], are synthetic alternatives to natural receptors that possess recognition properties similar to their natural counterparts (antibodies, receptors), but share the robustness and integrability to sensing devices typical of the polymeric materials. MIPs can be prepared towards a wide spectrum of analytes, ranging from small molecules to proteins [2] and can be shaped in formats from micron- to nano-dimensions. Over the last few years the downsizing of the MIPs to nanoMIPs has shown to bring significant advantages in terms of binding kinetics, accessibility of the binding sites, homogeneity of the imprints, quasi-protein-sized dimensions, strengthening further their resemblance to natural receptors. Thus, nanoMIPs appears as “plastic antibodies” [3] and are foreseen as ideal to be integrated to sensors [4]. Here MIP nanogels of varied compositions were synthesized and characterized for size, zeta potential and solvent-responsive properties. MIP nanogels were then coupled to plasmonic D-shaped plastic optical fibre (POF) [5], this latter chosen for the versatility of configurations offered, the easy and low cost of manipulation, the great numerical aperture, the large diameter, the possibility to withstand smaller bend radii than glass, the use of white light sources and the remote interrogation. Experimental evidences showed that the solvent-responsible nanoMIPs when combined to the POF platform enabled to modulate the optical response just by exploiting the solvent-induced conformational rearrangements of the nanoMIP, that occurs right at the proximity of the plasmonic surface. These responsive nanoMIPs permitted to actively modulate the resonance wavelength shifts, hence the optical signal, alike a polymer switch.

Solvent induced deformations of the MIP nanogels represent a reversible polymer switch



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OC4

Complex polyester-PEG nanoparticles as drug nanocarriers for targeting malignant brain tumors

Wanda Celentano,[a,b] Francesco Cellesi[a]

[a] Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, via Mancinelli 7, 20131, Milano, Italy

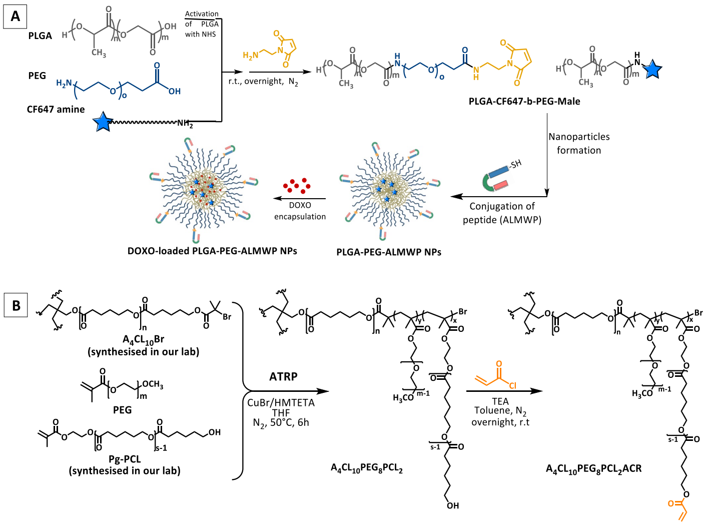
[b] Humanitas Research Hospital, via Manzoni 56, 20089, Rozzano (MI), Italy

wanda.celentano@polimi.it

Abstract

A major problem in nanomedicine is to enhance drug delivery across biological barriers, which prevent undesired access of external molecules to sensitive cells, organs and tissues. Recently, polymers with complex macromolecular architectures have found promising applications in drug delivery, especially as nanocarriers to encapsulate drugs or biological active agents. Commercial Poly(lactic-co-glycolic acid) (PLGA) and functionalized Poly(ε-caprolactone) (PCL) can be used in combination with poly(ethylene glycol) (PEG), to achieve aqueous dispersions of nanoparticles (NPs) of tuneable size. PLGA and PCL are biocompatible and biodegradable polymers, already approved by FDA (Food and Drug Administration) and EMA (European Medicines Agency) in various drug delivery systems [1,2]. In this study, free radical polymerization (FRP) and controlled polymerizations such as Ring Opening Polymerization (ROP) and Atom Transfer Radical Polymerization (ATRP) [3] were combined to obtain bioactive and traceable NPs, which were developed to target glioblastoma (the most common type of malignant brain tumor among adults) [4]. Fluorescent PLGA-PEG nanoparticles loaded with doxorubicin (DOXO) were functionalised with a targeting peptide (Figure 1A). In particular, an Activable Low Molecular Weight Protamine (ALMWP)-based peptide was selected for conjugation, since it can be activated mainly by glioblastoma cells. PCL and PEG were also used as building blocks to obtain a library of comb-like and start amphiphilic polymers, which are capable of forming ultrasmall nanoparticles, self-assembled as unimolecular micelles [5]. Different percentage of PEG and PCL were co-polymerized through ATRP, using multi-arm or linear macroinitiators. (Figure 1B). Functional nanoparticles were obtained in aqueous media through a standard nanoprecipitation method. Afterwards, they were functionalized with the ALMWP peptide through Michael type addition. Finally, DOXO was efficiency encapsulated and released *in vitro.* Biological tests confirmed a safe cytotoxic behavior and a triggered uptake of the nanoparticles by glioblastoma cell lines.

Figure 1. Synthesis of polymers and nanoparticles formation



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OC5

Radiative heat barriers for the fire protection of polyamide 6

Anne-Lise Davesne,[a] Fabrice Parent,[b,c] Johan Sarazin,[a] Tsilla Bensabath,[a] Séverine Bellayer,[a] Frédéric Sanchette,[b,c] Fabienne Samyn,[a] Maude Jimenez,[a] Serge Bourbigot[a]

[a] Université de Lille, ENSCL, UMR 8207, UMET, Unité Matériaux et Transformations, F 59 000 Lille, France

[b] ICD LASMIS, Université de Technologie de Troyes, UMR6281, CNRS, Antenne de Nogent, Pôle Technologique de Haute-Champagne, 52800 Nogent, France

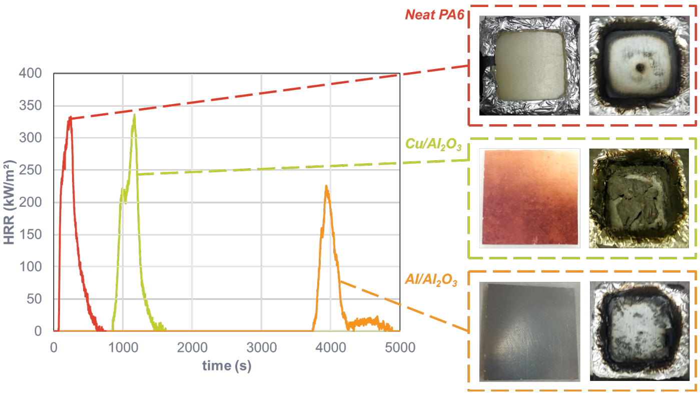
[c] NICCI, LRC CEA-ICD LASMIS, UTT, Antenne de Nogent-52, Pôle Technologique de Haute-Champagne, 52800 Nogent, France

anne-lise.davesne@univ-lille.fr

Abstract

Thin coatings are seen as effective fire resistant approaches to fireproof flammable substrates and have been attracting great attention since several decades. Indeed, they can act as a primary barrier for the heat and mass transfer driving the combustion process, without impacting significantly the properties of the material. More specifically, they can act as radiative heat barrier if they are designed to reflect infrared rays. This is of particular interest since radiative heat transfers are dominant in medium to large scale fire [1], contributing largely to the increase of temperature and the ignition of combustible materials. Highly reflective surfaces are easily obtained with very thin metallic layers, thanks to their high density of free electrons. Topped with a transparent refractory dielectric layer to protect it from environmental and high temperature corrosion, they make very efficient mirrors for a large range of visible and infrared wavelengths. This principle has been widely applied for aerospace and energy saving application [2], but scarcely for fire protection, despite early studies demonstrating their interest [3,4]. They found that using low-emissivity coatings increases the time to ignition of polymers by several order of magnitude under a radiative thermal constraint. On the downside however, no influence on the fire behavior was found. In this study, metal/dielectric coating (about 500 nm thick) were deposited on polyamide 6 substrates by pulsed DC magnetron sputtering. Their fire behavior was evaluated by cone calorimetry under a radiative heat flux of 50 kW/m², which corresponds to a fully developed fire. A thermocouple was embedded on the backside of the sample to monitor temperature changes and to evaluate the barrier effect of the coating. At first, different types of coatings (Al/Al_2O_3, Cu/Al_2O_3 and Al/AlN) were examined. All systems reduced heat absorption and consequently increased the time to ignition. However, using aluminum instead of copper for example, increases the performance of the coating. Indeed, the time to ignition was brought from 80 s for a neat polymer to more than one hour with Al/Al_2O_3, whereas copper only raised the time to ignition to 15 min. Each time, no influence on the burning behavior of PA6 was observed. To counterbalance this disadvantage, PA6 was filled with a commercial fire retardant (FR) additive to combine both surface and bulk mechanism. A complementary effect was obtained associating the long time to ignition brought by the low emissivity Al/Al_2O_3 coating and a strong reduction of the Peak of Heat Release Rate (by 50%) brought by the FR additive.

Mass loss cone calorimetry results: Heat Release Rate as a function of time of neat PA6 (red line), Cu/Al_2O_3-coated PA6 (green line) and Al/Al_2O_3-coated PA6 (orange line)



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OC6

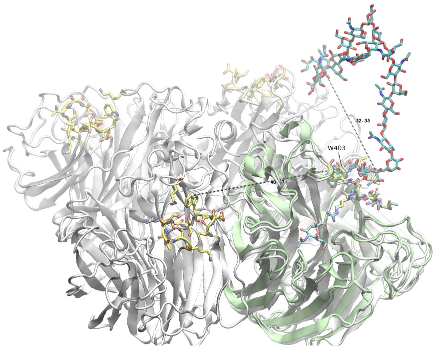
MD simulation of the interaction between neuraminidase N1 of the 1918 pandemic influenza virus to sialoglycan

Stefano Elli,[a] Nicola Gambacorta,[a] Mikhail Matrosovich,[b] Marco Guerrini[a]
[a] Istituto di Ricerche Chimiche e Biochimiche "G. Ronzoni", via G. Colombo 81, 20133, Milano, Italy
[b] Institute of Virology, Philipps University, Hans-Meerwein-Str.2, 35043 Marburg, Germany
elli@ronzoni.it

Abstract

Wild aquatic birds and domestic poultry represent the major reservoir of influenza A viruses (IAVs). These viruses occasionally acquire the ability to infect humans, potentially generating dangerous pandemic events [1]. IAVs contain two major surface glycoproteins, the hemagglutinin (HA) and the neuraminidase (NA), both able to recognize the sialic acid moiety at the non-reducing end of glycoconjugate chains decorating the surface of the target cells. The HA mediates virus binding to the cell surface receptors and fusion of the viral and cellular membranes; the NA has a more complex and less understood function [2]. Thus, the NA enzymatically desialylates cellular and extracellular glycoconjugates in the epithelium, helping the virus entry into naïve cells [3] and facilitating the release of the virus progeny from the membrane of the infected cells. A functional balance between the receptor-binding activity of the HA and receptor-destroying activity of the NA is essential for efficient virus replication [4,5]. The discovery of a second sialic acid binding site (hemadsorption site, HAD) located in proximity to the catalytic site in N9 NA [6] and NAs of other avian IAVs contributes to the complexity of the NA function. The biological role of the HAD site is still under debate, although limited evidence suggests that HAD site facilitate the NA enzymatic degradation of polyvalent glycans on the cell surface and extracellular mucus [7,8]. The aim of this study is to characterize the interaction between the HAD site of the NA of the 1918 pandemic influenza virus A/BREVIG MISSION/1/1918 (H1N1) (PDB ID 3B7E) and oligosaccharides mimicking its natural sialoglycan substrates using the "state of the art" MD simulation. The molecular recognition specificity of HAD site toward a2-3 and a2-6 Neu5Ac-Gal terminated glycans (avian- and human-type receptors, respectively) will be considered, the free energy of binding will be estimated using the MMPBSA [9] approach, and these results will be compared to HADs of different NAs. The possibility that poly-valent terminated receptors binds HAD site of NA will be considered starting from a conformational analysis of these macromolecules as described by MD simulation [10]. This investigation will improve the knowledge on the molecular mechanisms of the IAV infection, potentially contributing to the design of new anti-viral drugs.

Multi-valent sialoglycan binding N1 3B7E tetramer



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Acknowledgments

Istituto di Ricerche Chimiche e Biochimiche "G. Ronzoni" via G. Colombo 81, 20133, Milano, Italy.

OC7

Controlled synthesis of linear polyamidoamino acids and preliminary investigation on their cytocompatibility and application in photodynamic therapy

Federica Ferruti,[a,b] Jenny Alongi,[a] Amedea Manfredi,[a] Elisabetta Ranucci,[a] Paolo Ferruti[a]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy

[b] Current address: Dipartimento di Scienza dei Materiali, Università di Milano – Bicocca, via R. Cozzi 55, 20125, Milano, Italy

f.ferruti@campus.unimib.it

Abstract

Polyamidoamino acids (PAACs) are biocompatible synthetic polymers obtained by Michael-type polyaddition of bisacrylamides with natural α-amino acids, which preserve both their chirality and their amphoteric character in the final product [1]. The resulting macromolecules assume chirality-related, stable, pH dependent conformations in aqueous media [2]. These promising features suggest potential for PAACs application in biomedicine and pharmaceutics. Their synthesis is usually simple and environmentally friendly but results in highly polydisperse polymers endowed with random aminoacidic sequence when using α-amino acids mixtures. In order to be acknowledged as active components in pharmaceutical formulations, PAACs should have a definite molecular weight and structure. The aims of the present work are to set up a synthetic strategy to obtain PAACs with controlled structure and molecular weight by means of a step-by-step synthetic process [3] and the use of macromonomers and to preliminarily explore the biomedical applications of these polymers. Despite their intrinsic slowness, the synthetic tactics here proposed present the advantages of being run in aqueous media without release of by-products and with no need for added catalysts, protection/de-protection steps, soluble or solid supports. The step-by-step synthesis is based on the different reactivity of the amine hydrogen atoms of α-amino acids in the Michael addition with activated double bonds [4] and the poor solubility of α-amino acids and their addition products in organic solvents. In order to demonstrate the feasibility of this process, the controlled synthesis of the PAAC from *L*-arginine and N,N'-methylenebisacrylamide was pursued up to a monodisperse product presenting 11 monomeric units and molecular weight 1814. The same synthetic procedure was also tested with *L*-alanine. All intermediates were isolated and characterized. Each of them was α,ω-difunctionalized with either acrylamide or sec-amine functional group and, therefore, they could be used as macromonomers to synthesize complex macromolecular architectures. In a first instance, polymers with controlled sequences of amino acid- and amino- units were prepared. In particular, some *L*-arginine containing building blocks α,ω-terminated with acrylamide functions were copolymerized with primary amines (ethylamine), bis-secondary amines (piperazine), α-amino acids (glycine, *L*-alanine, *L*-arginine) and building blocks α,ω-terminated with amino acidic (*L*-alanine and *L*-arginine) moieties. After a single ultrafiltration step, all polymers resulted narrowly monodisperse, probably due to the relatively high molecular weight of the monomers included in the polymer structure. A family of narrowly polydisperse, sequence controlled polymers based on N,N'-methylenebisacrylamide, piperazine and different arginine stereoisomers was synthesized. They underwent toxicity and cell internalization tests as potential siRNA transfection agents with promising results. Moreover, a new class of PAAC-based photodynamic therapy agents able to sensitize singlet oxygen production for noninvasive cancer therapy was developed. A structure-controlled, *L*-arginine containing PAAC with a phenanthroline pendant could stably coordinate Ru(II). The complex ability to sensitize singlet oxygen generation was investigated. In conclusion, the strategies here presented allow to obtain narrowly polydisperse PAACs with a fine molecular weight and structure control showing outstanding cytocompatibility and potential in biomedicine.

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OC8

Zein: a versatile and promising natural polymer for drug delivery applications

Agnese Gagliardi,[a] Francesca Froiio,[a] Donatella Paolino,[a] Sonia Bonacci,[b] Antonio Procopio,[b] Christian Celia,[c] Massimo Fresta,[b] Donato Cosco[b]

[a] Department of Experimental and Clinical Medicine, University of Catanzaro “Magna Græcia”, Campus Universitario “S. Venuta”, 88100, Catanzaro, Italy

[b] Department of Health Sciences, University of Catanzaro “Magna Græcia”, Campus Universitario “S. Venuta”, 88100, Catanzaro, Italy

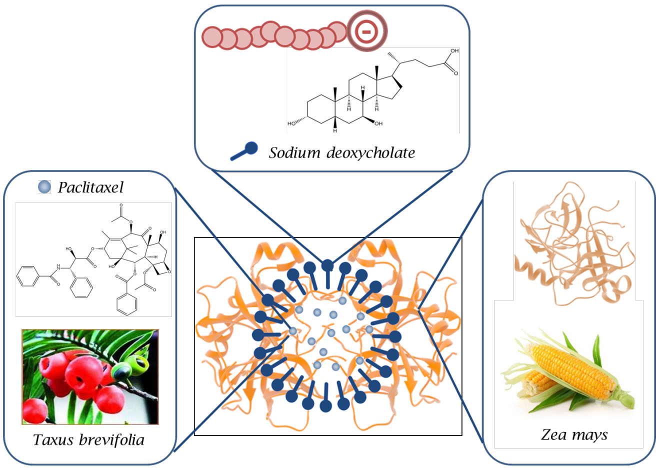
[c] Department of Pharmacy, University of Chieti - Pescara “G. d’Annunzio”, via dei Vestini 31, 66100, Chieti, Italy

gagliardi@unicz.it

Abstract

In the field of controlled drug delivery plant proteins have aroused a great interest in comparison with synthetic or semisynthetic polymers thanks to their features of availability, bio- and cyto-compatibility and poor immunogenicity. In detail, zein, a versatile hydrophobic protein abundantly contained in corn, has been used in order to develop hydrogels, films, nanoparticles for food-, biomedical, and drug delivery applications. In particular, our research team recently demonstrated that it is possible to combine raw zein and sodium deoxycholate with the aim of obtaining high stable colloidal systems [1]. The anticancer drug paclitaxel (PTX) was efficiently retained by the polymeric matrix and the obtained zein nanoparticles have been characterized by a mean diameter of ~150 nm. The nanosystems containing PTX demonstrated suitable storage stability and were not destabilized by temperatures up to 50 °C, pH alterations, the freeze-drying process or incubation with serum proteins. Moreover, the nanoencapsulation of the anticancer agent promoted a greater decrease in cell viability as compared to the free form of PTX at all the concentrations used; the best cytotoxicity was exerted by the colloidal formulation containing the lipophilic drug on the MCF-7 cells. The uptake of the nanosystems containing PTX could be a plausible explanation for the increased cytotoxic effect of the bioactive; in fact, the evaluation of the cell interaction rate of tritiated zein nanoparticles confirmed a time-dependent cell uptake of the polymeric carriers that occurred after only 1 h incubation. The use of zein nanoparticles also precludes the use of organic solvents to solubilize the lipophilic compound, which would mean a potential dramatic decrease in the side effects related to their use in human beings [2]. Furthemore, raw zein dispersed in a water/ethanol solution was used to develop and characterize various formulations as a function of the protein concentration with the aim of providing a panel of different gels useful for food, biomedical and drug delivery applications. In particular, our research team investigated the physico-chemical characterization of zein-based gels through passive and dynamic microrheology [3]. The stability of the samples was determined at 25 °C and 37 °C by a Turbiscan Lab apparatus due to the different gelation properties of the various formulations. The samples containing 15% and 20% w/v of zein formed stable dispersions especially at 37 °C. The high protein concentration showed storage moduli values significantly greater than those of viscous moduli, demonstrating that the elastic character became dominant. The viscosity of these samples decreased as the shear rate increased, thus demonstrating a typical pseudoplastic behavior. These results highlight the peculiar properties of zein formulations prepared with 15% and 20% w/v of protein that can be used as a protective coating for fresh foods avoiding or decreasing their deterioration. Moreover, they can be potentially used for several applications as a film to modulate the release profiles of various bioactive compounds.

Schematic representation of PTX- loaded zein nanoparticles



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OC9

Disulfide restructuring on nanomanufactured polymer particles

Mike A. Geven,[a] Hanying Luo,[b] Donghun Koo,[b] Gangadhar Panambur,[b] Roberto Donno,[a] Arianna Gennari,[a] Roberto Marotta,[c] Benedetto Grimaldi,[d] Nicola Tirelli[a]

[a] Laboratory of Polymers & Biomaterials, Fondazione Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy

[b] Material Science department, MilliporeSigma, Sigma-Aldrich Corp., 3050 Spruce St, St. Louis, MO, 63103, USA

[c] Electron Microscopy Facility, Fondazione Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy

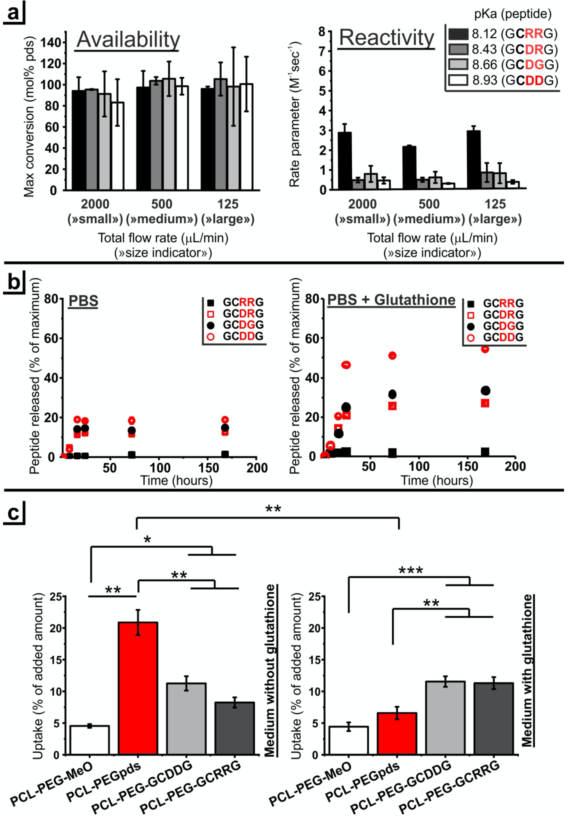
[d] Laboratory of Molecular Medicine, Fondazione Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy

mike.geven@iit.it

Abstract

In drug delivery, nanoparticles can positively affect both pharmacokinetics and pharmacodynamics of a drug, by prolonging its circulation time, by allowing preferential accumulation and by trafficking it across biological barriers. Critical for the nanoparticle performance are both the values and the reproducibility of parameters such as average size, size dispersity, geometry and surface chemistry [1]. In this work, we investigated two essential points in the preparation of surface-functionalized nanocarriers. A) The controlled production in a microfluidic-assisted fashion, using poly(ε-caprolactone)-b-poly(ethylene glycol) with a thiol-exchangeable pyridyl disulfide group (pds) on the PEG-terminus (PCL-PEGpds). B) The stability of a disulfide-based bioconjugation on the nanoparticle surface in biologically relevant conditions. Particles of PCL-PEG-methoxy (PCL-PEG-MeO) and PCL-PEGpds (provided by Sigma Aldrich Corp., 5.5 kDa PCL, 6 kDa PEG) were prepared by mixing polymer in acetone with water in a microfluidics chip (Micromixer, Syrris Ltd.) (organic/water ratio = 0.5) with varying total flow rates (TFR). Particle size was determined by dynamic light scattering (DLS) and asymmetric flow field flow fractionation (AF4). The average particle size (DLS) can seemingly be controlled in the range of 80 to 160 nm, using the microfluidic TFR. In depth characterization by AF4, however, showed 20-60 nm particles to be the main constituent of all suspensions irrespective of the TFR value. Peptides (from Biomatik Corp.) with ionic residues (double positive RR, neutral RD, anionic DG and double negative DD) flanking a cysteine were then reacted with particles of PCL-PEGpds (peptide/pds = 3 mol/mol) at 37 °C in PBS. During the reactions, pds release kinetics were monitored via UV-Vis. The TFR at which the particles were formed (and thus average particle size found in DLS) did not affect the availability and reactivity of pds groups on PCL-PEGpds particles (figure 1a). On the contrary, their reactivity was strongly dependent on the peptide thiol pKa. The thiol pKa furthermore determined stability of the resulting disulfide, as shown in peptide release experiments in PBS and PBS containing glutathione (monitored via HPLC). The peptides formed more stable disulfides with increasing thiol acidity resulting in slower release (figure 1b). Importantly, even the most rapidly exchangeable disulfides (double negative DD peptide) were stable for several hours, differently from pds, which can rapidly exchange with glutathione. Internalization of particles comprising PCL-PEG-MeO, PCL-PEGpds and PCL-PEGpds reacted with double positive (RR) and double negative (DD) peptides were studied over two hours with HCT116 cells. All particles were loaded with pyrene to evaluate fluorescence in cell lysates. The particle uptake by HCT116 (figure 2c) reflected the stability of the peptide functionalization, with the presence of glutathione only affecting the uptake of pds-containing particles. These results show that A) thorough size control and characterization is of utmost importance when processing functional nanoparticles, and B) controlling the stability of (disulfide-based) functionalization on microfluidic prepared nanoparticles is of importance for the biological performance of the particles.

Figure 1. (a) Reaction parameters for peptides with PCL-PEGpds particles formed at different TFR, (b) peptide release profiles from particles and (c) uptake of particles by HCT116



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OC10

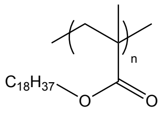
Thermo-optically responsive solid-solid phase change materials as passive temperature controlling building enclosures

Sergio Granados-Focil,[a] Pramod Mishra,[a] Amy Chen,[b] Mingjiang Tao,[b] Steven Van Dessel[b]
[a] Gustaf Carlson School of Chemistry and Biochemistry, Clark University, Worcester, MA, USA
[b] Civil Engineering Department, Worcester Polytechnic Institute, Worcester, MA, USA
sgranadosfocil@clarku.edu

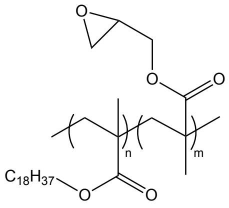
Abstract

Stimuli-responsive coatings based on Solid-Solid phase change materials (SS-PCMs) have been synthesized and evaluated for their use in passive temperature-controlling building enclosures. The transparency of these coatings changes as a function of temperature, enabling the design of building enclosures capable of regulating their reflectivity as a function of temperature, thus increasing the efficiency of the thermally regulating layer [1]. The polymeric matrices were synthesized by radical polymerization of mixtures containing a crosslinkable motif, a mechanically-reinforcing monomer and a polymerizable phase-changing motif. The effect of matrix composition on the heat-storing capacity and the temperature-responsive optical contrast will be described. The introduction of up to 5% molar equivalents of mechanical reinforcer produces films with enhanced flexibility while maintaining relatively high heats of melting. Addition of crosslinkable moieties ranging from 3% to 10% molar equivalents produced form-stable SS-PCMs with latent heats ranging from 110 J/g to 80 J/g. A series of solvent- and porogen-mediated foaming protocols were tested and evaluated as optimal methods to produce large area porous coatings. Optimized compositions can generate coatings with latent heats above 100 J/g and temperature-dependent transmission contrast ratios higher than 800:1. These properties confirm our finite-element calculations indicating that incorporation of these "smart" coatings into building enclosures is a promising path to the development of more energy efficient buildings [2]. This study provides the experimental data on polymeric SS-PCMs that is required to close the design loop and produce working prototypes of these building envelopes.

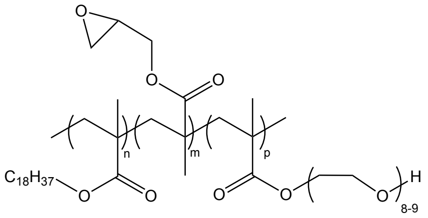
Chemical structure and properties of thermally crosslinked SS-PCMs



PSMA



PSMA-PGA



PSMA-PGA-PEGMA

PCM material$^{\#}$	ΔH_m (J/g)	T_m (°C)	Melting transition*
PSMA^{XL}	72	52-66	S-S
PSMA-PGA$_{(90-10)}$	83	51-61	S-L
PSMA-PGA^{XL}	80	51-62	S-S
PSMA-PGA-PEGMA^{XL}$_{(85-10-5)}$	84	51-63	S-S
PSMA^{XL} / E2S2 [90/10]	97	52-61	S-S
PSMA-PGA$_{(90-10)}$ / E2S2 [70/30]	107	51-61	S-L
PSMA^{XL} / E2S2 [70/30]	120	52-62	S-S
PSMA-PGA-PEGMA^{XL}$_{(85-10-5)}$ / E2S2 [70/30]	112	50-63	S-S

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OC11

Dynamic mechanical characterization of cured NR/BR compounds: including investigations into the effects of mastication time and different peptizers

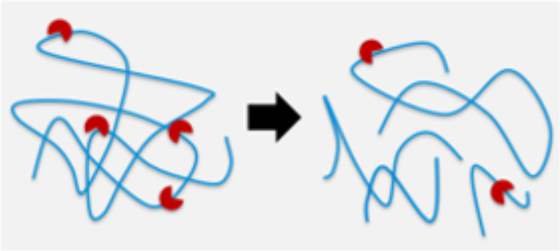
Muhammad Haris,[a] Sadegh Behdad,[b] Troy Nickel,[b] Marco Coletti[c]
[a] TA Instruments, Applications Laboratory, Wetzlar, Germany
[b] TA Instruments, Applications Laboratory, Minnesota, USA
[c] TA Instruments, divisione di Waters Italia, Sesto San Giovanni (MI), Italy
mharis@tainstruments.com

Abstract

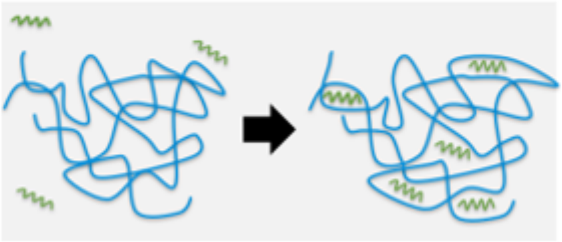
Physical and structural properties of vulcanized rubber can be characterized by dynamic mechanical testing methods, including, but not limited to, Dynamic Mechanical Analysis. This study outlines the effect of addition of two distinctly different peptizers added in uncured rubber to assist the dispersion of various ingredients such as filler, accelerator, inhibitor, activators and vulcanizing agents. Consistent tan-del peaks and a slight change in molecular weight distribution were reported through temperature sweeps. Broadening of molecular weight distribution was a direct result of chain scission action of chemical peptizers. All the samples exhibited Payne effect due to failing Van der Waals interactions as filler-filler spacing increased at higher strains. Additionally, more mastication time led to the rise of loss modulus in all samples suggesting increased free volume. When samples were subjected to mechanical ageing, higher mastication time and chemical peptizers registered greater relative change in elastic response and loss factor. Furthermore, heat buildup tests revealed material's real time response under application related dynamic loading. Samples with chemical peptizers exhibited higher temperature compared to physical peptizers. Chemical peptizers and higher mastication time gave inferior blow out performance whereas physical peptizers and lower mastication time showed better blow out performance of all. These results indicate that peptizers have an influence on final material viscoelastic properties in additional to their primary role in assisting in mixing during mastication and physical peptizers offer optimum solution to mixing without sacrificing final properties.

Working principle of each peptizer

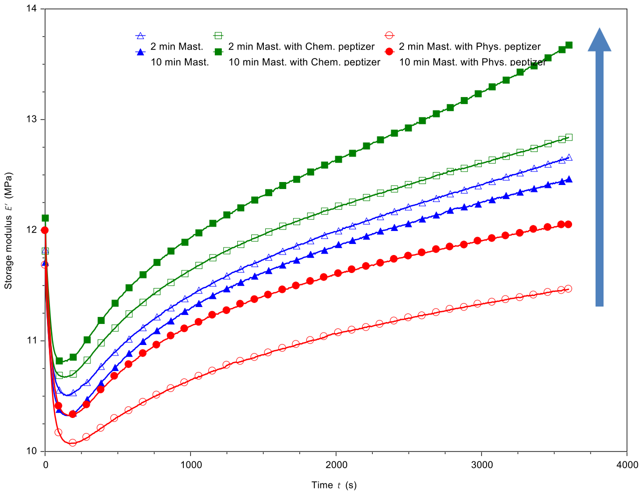
Chemical Peptizers: Chain scission



Physical Peptizers: Chain lubrication



Storage moduli vs time during heat buildup



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OC12

Is a molecular “traffic warden” the solution to control drug delivery from polymer-based nanocarriers?

Lorella Izzo,[a] Massimo Mella,[b] Enrico Caruso,[a] Miryam C. Malacarne,[a] Stefano Banfi[a]

[a] Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell’Insubria, via J.H. Dunant 3, 22100, Varese, Italy

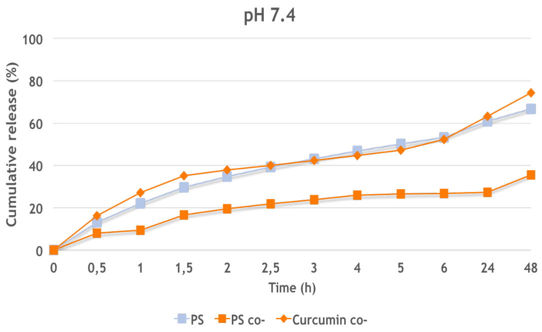
[b] Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell’Insubria, via Valleggio 9, 21100, Como, Italy

lorella.izzo@uninsubria.it

Abstract

Polymers-based nanocarriers, such as micelles or polymersomes, are designed to transport active molecules in the body keeping the drug inside until the target tissue is reached in order to enhance bioavailability and reduce side effects. Nanocarriers co-delivery strategy is often used as synergistic therapy and has recently made substantial progress e.g. to overcome drug resistance [1] or for specific and personalized theranostics [2]. Importantly, an active molecule may possess chemical groups able to interact with the polymer chains of the nanocarrier possibly inducing structural modifications of the latter and consequently influencing the release kinetic of a second co-loaded species. This study concerns the effect of curcumin on the kinetic of release of two active molecules, a hydrophobic photosensitizer and the hydrophilic ampicillin sodium salt, encapsulated into two different nanocarriers, namely biodegradable micelles based on polylactide [3] and pH-sensitive polymersomes based on poly(dimethylaminoethyl)methacrylate [4,5] respectively. In both cases, it was found that curcumin is indeed able to reduce rate and amount of the second-molecule release, probably with a mode of action depending on both the chemical nature of copolymers forming the nanocarrier and of the co-loaded active molecule. When adsorbed into the pH-sensitive nanocarrier, the effect is likely induced by the formation of strong hydrogen bonds between the phenolic hydroxyls of curcumin and the amino pedant groups of polymers, as evidenced by IR-spectra. Such interaction may be able to “protect” polymersomes against the proton osmotic pressure reducing the ampicillin release over time. The effect of curcumin on the release of the hydrophobic photosensitizer from polylactide-based micelles, instead, may be probably due to interactions between the co-loaded molecules rather than curcumin and polymer chains. In fact, analyses show the possible formation of a complex, at least at pH 7.4, between the deprotonated curcumin and the zwitterionic photosensitizer. In the whole, the reported experimental results appear to provide important indications when it comes to formulate co-loaded drug delivery systems based on polymer nanocarriers. It seems possible to choose drugs for a combination therapy that might be appropriate not only for the therapeutic outcome but also for the modification of kinetic release of molecules provided in an appropriate polymer-based nanocarrier. Besides, it is possible to use an active molecule to modulate the release of a second one at different pH and to reduce or to avoid it when needed e.g during drugs transport in the blood at pH 7.4. In our specific cases, curcumin seems to work as a molecular “traffic warden” able to control desorption of molecules from nanocarriers, both polymersomes and micelles. More in general, this study evidences how a deeper insight into the physico-chemical interactions among the different parts of a drug delivery system, i.e. the nanocarriers forming copolymers and the co-loaded active molecules, may pave the way toward a rationally improved formulation for a controlled, precise and personalized release.

Release profile of a photosensitizer (PS) loaded and co-loaded with curcumin in mPEG(PLLA)$_4$ based micelles



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OC13

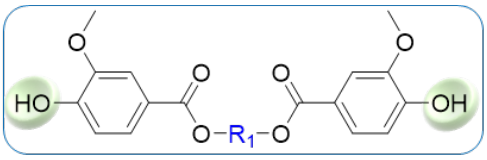
Solvent-free synthesis of new fully biobased diol monomers through industrially viable approach: Toward new insights into the valorization of vanillic acid-based polyesters

Nejib Kasmi, George Z. Papageorgiou, Dimitrios N. Bikiaris
Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Greece
nejibkasmi@gmail.com

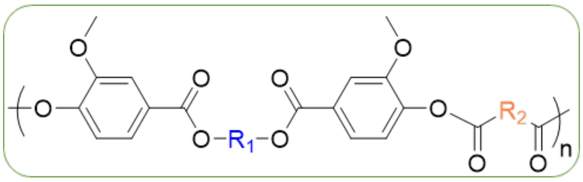
Abstract

This study spotlighted a facile and greener solvent-free synthetic process, successfully carried out herein, to prepare three novel 100% renewable resources-based monomers derived from vanillic acid. The latter showed an excellent thermal stability and high melting points ranging between 121 °C and 142 °C. To ascertain their stability toward the conditions of melt polycondensation (high reaction temperature and metal-based catalyst), these environmentally friendly diols were subjected to melt polycondensation with diacyl chlorides having different length alkane bridges under catalyst-free conditions and also with a stiff building block, namely dimethyl furan-2,5-furan dicarboxylate (DMFD), in presence of TBT catalyst. Results attained in this report indicate that all resulting polyesters are wholly amorphous materials and they revealed satisfactory viscosity values. These new samples, which were duly characterized in detail by ^{1}H, ^{13}C NMR and FTIR spectroscopies, possess good thermal stability depending on their chemical composition with onset degradation temperatures $T_{d,5\%}$ oscillating between 314 and 373 °C and a very wide glass transition temperature T_g range (-2.8 ÷ 69 °C). The overall conclusion is that such work is a concrete contribution as a support and helpful reference to highlight the feasibility of a more environmentally benign solvent-free pathway for sustainable building blocks design. This fruitful synthesis route that could be readily applied at industrial scale makes the development of fully biomass-derived plastics easier and faster, thereby achieving a greener future through smoothing the way for moving forward in transition from fossil fuels to a bio-based economy, which is the real willingness of both the scientific and industrial communities.

Synthesis route of new three vanillic acid-based diol monomers



Synthesis route of new fully renewable polyesters from vanillic acid-based diols



OC14

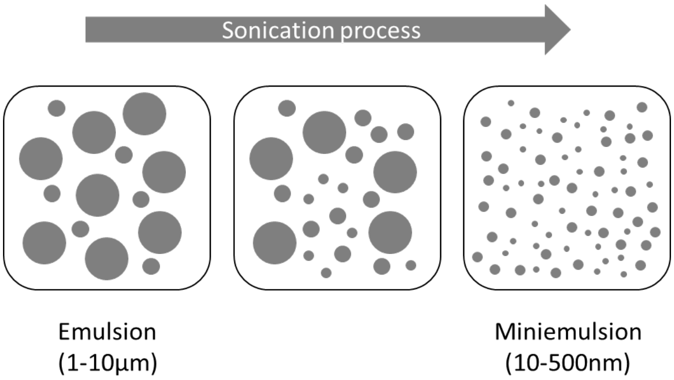
Miniemulsion techniques to include hydrophobic monomers in water based acrylic polymer dispersions

Marino Malavolti, Marco Cerra, Tito Zanetta, Claudio Re, Dario Smacchia
R&D Department, Vinavil S.p.A., via Toce 7, 28844, Villadossola (VB), Italy
m.malavolti@vinavil.it

Abstract

Polymerization in water dispersed systems (emulsion) has many advantages: it keeps a low viscosity of the mixture and allows an efficient heat reaction removal. Moreover, water is a nontoxic, environmentally friendly and inexpensive solvent. However, this polymerization process involves a mass transfer of monomer from the emulsion droplets (1-10 µm) to the monomer-swollen micelles (10-20 nm), where the polymer growth take place, therefore the hydrophilic/hydrophobic nature of the monomer plays a key role. In miniemulsion the droplets are so small (and so many) that the initiator (or a small radical) can be absorbed and perform the polymerization inside them, limiting all the mass transfer processes and allowing, for example, incorporation of very hydrophobic monomers or encapsulation of inorganic solids. The main drawback of miniemulsion is the high amount of energy required to brake-up the emulsion in submicron droplets and increase the interfacial area. Typical laboratory equipment are rotor-stator systems, sonifiers and high-pressure homogenizers [1,2]. In this work we used sonication to produce a quite stable miniemulsion of a hydrophobic monomer (stearyl acrylate or stearyl methacrylate) to produce latexes for hydrophobic coatings.

Miniemulsion preparation scheme



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OC15

Hydrophobic polyamidoamines: a new class of technological materials?

Massimo Marcioni,[a,b] Barbara Immirzi,[c] Giovanni Dal Poggetto,[c] Elisabetta Ranucci,[a] Paolo Ferruti,[a] Jenny Alongi,[a] Amedea Manfredi[a]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy

[b] Current address: Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria Campus, via Teresa Michel 5, 15121, Alessandria, Italy

[c] Institute for Polymers, Composites and Biomaterials CNR, via Campi Flegrei 34, 80078, Pozzuoli (NA), Italy

massimo.marcioni@polito.it

Abstract

Polyamidoamines (PAAs) are synthetic, biocompatible and biodegradable polymers obtained by the Michael-type stepwise polyaddition of *prim*- or *sec*-amines with bisacrylamides. PAAs have shown potential application in the biomedical field, such as drug and protein intracellular carriers, transfection promoters, antiviral, antimalarial agents and, in hydrogels form, as scaffold for tissue engineering [1]. However, PAA hydrogels are not suitable as implantable materials due their poor mechanical properties. Different approaches were investigated to overcome this problem, as the preparation of composites with inorganic fillers or PLLA mats [2,3]. The new approach reported in this work is based on the development of hydrophobic, semi-crystalline PAAs with sufficient mechanical strength to be used as hydrogel supports. Hydrophobic PAAs were prepared from long chain aliphatic bisacrylamides and different diamines. In particular, the monomers employed were: as for the bisacrylamides, N,N'-hexamethylene-bisacrylamide (HEXAMBA), N,N'-octamethylene-bisacrylamide (OMBA), N,N'-decamethylene bisacrylamide (DMBA) and N,N'-dodecamethylene bisacrylamide (DDMBA), obtained by the Schotten-Baumann reaction involving acryloyl chloride and 1,6-diaminehexane, 1,8-diamineoctane, 1,10-diaminedecane or 1,12-diaminedodecane, respectively; as for the amine monomers, piperazine (PIP), N,N'-dimethyl-1,6-hexanediamine (DMHEXA), N,N'-dimethyl-1,2-ethanediamine (DMEDA*sym*), N,N-dimethyl-1,2-ethanediamine (DMEDA*as*), N,N'-dibenzyl-1,2-ethanediamine (DBEDA) and N,N'-diethyl-1,2-ethanediamine (DEEDA). The polymerization reactions were first performed in benzyl alcohol solution, for two days at 60°C. The products were retrieved by precipitation with excess diethyl ether. All PAAs were characterized by FT-IR/ATR and NMR spectroscopies. DSC and TGA calorimetric analyses were performed to investigate the thermal properties of the hydrophobic PAAs. All PAAs exhibited good thermal stability, with decomposition onset temperatures ≥ 200 °C and were semi-crystalline. The amine moieties seem to exert the main influence on the thermal properties of the final product. For instance, being the bisacrylamide moiety the same, the melting points range from 195 °C (DDMBA-PIP) to 50°C (DDMBA-DMEDA*as*). The bisacrylamide influence exists but is less evident. For instance, being the amine moiety the same, the melting points range from 80 °C (HEXAMBA-DMHEXA), to 100°C (DDMBA-DMHEXA). The mechanical properties were studied on thin films obtained by compression molding. On the whole, all polymers tested were successfully filmed. The best flexible and resistant films were those deriving from the DDMBA-based polymers, such as DDMBA-DMHEXA or DDMBA-DMEDAs. To settle a more sustainable process, a bulk polymerization process was preliminarily studied to prepare DDMBA-DMHEXA and OMBA-DMHEXA. The reaction was carried out under inert atmosphere and in the presence of a radical inhibitor at 140°C or 150°C for DDMBA-DMHEXA or OMBA-DMHEXA, respectively. Preliminary results showed that lower molecular weight, but comparable thermal properties were observed with respect to samples obtained with the solution process. In addition, the yield strength of DDMBA-DMHEXA was higher than that of OMBA-DMHEXA with 10.14 ± 0.58 MPa and 4.72 ± 1.43 MPa, respectively.

DDMBA-DMHEXA film

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OC16

Weakly polyelectrolytic surfaces: are there important interactions between ionized and neutral tethered monomers?

Massimo Mella,[a] Stefano Vaghi,[a] Lorella Izzo,[b] Andrea Tagliabue,[a] Giovanni Vigliotta[c]

[a] Dipartimento di Scienza ed Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100, Como, Italy

[b] Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, via J. H. Dunant 3, 21100, Varese, Italy

[c] Dipartimento di Chimica e Biologia, Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy

massimo.mella@uninsubria.it

Abstract

Positively charging surfaces induces intrinsic bactericidal properties via a mode of action that fosters divalent cation leaching and consequent destabilization of the bacterial outer wall [1-3]. To effectively kill bacteria, surfaces must, however, bear a charge density in excess of 10^{15} charges/cm^2 [4]. When surface charges are induced by ionization (i.e protonation) of weakly basic groups tethered to polymeric plaques, charged-neutral (e.g. ammonium-amine) group interactions may modulate the extent of the ionization itself. Aiming to better comprehend the role played by polymer composition (i.e. the molar fraction of monomers bearing ionizable groups) in defining the electrolytic properties of polymeric surfaces, this study reports an investigation of such lateral interactions and how they impact on surface charge density. To do so, contact angle measurements have been initially employed to gauge surface wettability, which is a function of the surface charge density, versus the pH of buffer solutions, *de facto* titrating pendant amine groups tethered to poly-methacrylate based plaques (see Figure 1 for polymer details) [5]. Even though an increase in wettability is evidenced for all polymers upon lowering pH below 6, experiments failed to clearly differentiate polymers with different amount of surface pendants. This outcome is probably related to the limited extent of contact angle variation upon protonation, as the polymer surface appears quite wettable already at high pH. To deepen our understanding, ATR-IR spectroscopy was thus employed to gauge the change in relative amount of protonated amine groups (normalized with respect to their molar fraction) compared to the invariant ester group of the methacrylates versus pH; the fairly intense adsorption band of N-H bending was exploited for this task. From these results (Figure 2), it emerged that the normalized adsorption intensity of protonated groups at pH=7 is higher for polymers containing a lower amount of amine pendants, *de facto* suggesting a lower pK_b (i.e. a more marked ability to coordinate protons) for this species in neutral conditions. Considering that lowering further the pH until it reaches mildly acid conditions (pH=5) brings the relative normalize intensity in agreement with general expectations, the results at pH=7 appears at variance with theoretical results [6] suggesting a stronger basicity when stabilizing interactions between charged and neutral monomers are possible. The rationalization of such unexpected finding emerges considering the difference in bending frequency between a free ammonium and an ammonium-amine dimer, the latter vibrating roughly 100 cm^{-1} above the former as a consequence of the strongly directional nature of the charged hydrogen bond. This upward shift leads to a superposition between the N-H…N bending and the ester C=O stretching, *de facto* hiding the former and impeding a quantitative estimate of its population.

In conclusion, this work provides for the first time experimental support to the possible formation of lateral charged hydrogen bond interactions between ionizable pendants tethered to polymeric surfaces and how these depend on polymer composition. This finding thus indicates an additional parameter exploitable for a better design of ionizable polymeric surfaces.

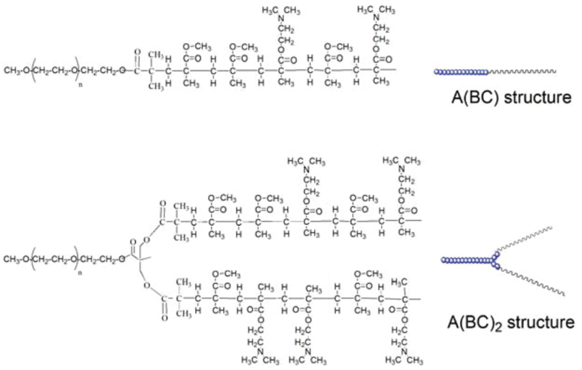

Figure 1: Structure of PEG-b-(ran-MMA-DMAEMA)$_n$ polymers used to prepare pH-responsive films and plaques. Polymer masses span the 30-70 KDa range; X_{DMAEMA} varies between 0.15 and 0.37; the PEG block has a constant mass of 2 KDa.

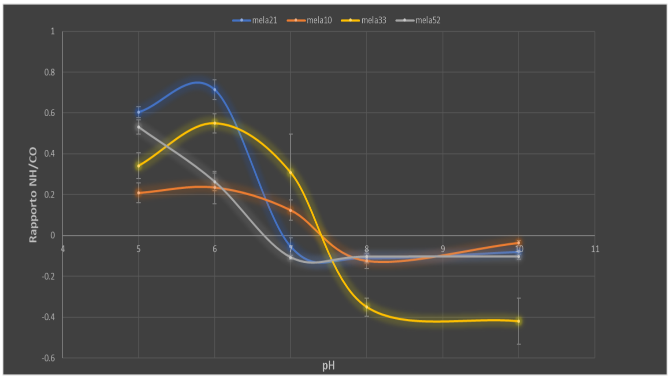

Figure 2: composition normalized N-H bending/C=O stretching adsorption ratio for PEG-b-(ran-MMA-DMAEMA)$_n$ polymers versus pH. Blue and grey lines, X_{DMAEMA}~0.35; orange and yellow lines, X_{DMAEMA}~0.16

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OC17

UV-induced synthesis of polyaniline (PANI)-TiO_2 composites: mechanistic insight and application as sorbent for wastewater remediation

Daniela Meroni,[a,b] Carolina Cionti,[a,b] Cristina Della Pina,[a,c] Ermelinda Falletta,[a,c] Silvia Ardizzone[a,b]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy

[b] Consorzio INSTM, via G. Giusti 9, 50121, Firenze, Italy

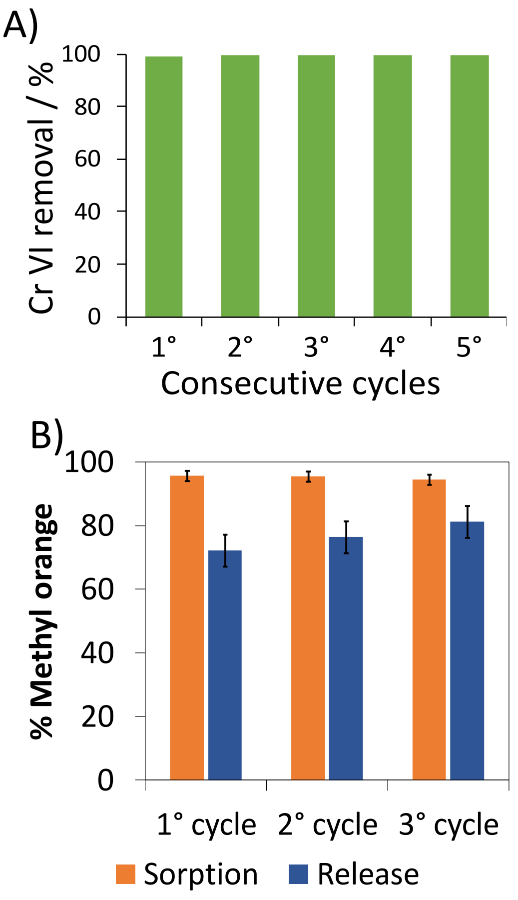
[c] ISTM-CNR, via C. Golgi 19, 20133, Milano, Italy

daniela.meroni@unimi.it

Abstract

In recent years, the application of PANI-based materials to pollutant abatement has been proposed owing to PANI environmental stability and excellent sorption capabilities [1]. However, conventional synthetic procedures of PANI-materials are based on toxic reagents and generate hazardous by-products and large amounts of inorganic waste. As an alternative to conventional PANI oxidative syntheses, we recently developed a green procedure starting from benign reactants ((*N*-(4-aminophenyl)aniline and H_2O_2) and initiated by light-irradiated titanium dioxide [2]. In order to unlock the full potential of this synthetic approach, we studied the relative roles of the oxide semiconductor and of H_2O_2 in this two-step synthetic approach. Composites were synthesized by varying the TiO_2:H_2O_2:aniline dimer molar ratios and were characterized from the compositional, structural, morphological, optical, and thermal point of view. Moreover, the reaction mechanism was investigated via a combination of spectroscopic and spectrometric techniques. We found that the first step is driven by TiO_2 and UV irradiation and leads to the formation of oligomers at the oxide surface, promoting a higher polymer crystallinity in the final composite. The polymer chain growth requires the addition of H_2O_2 and the added amount has a crucial role on the reaction pathway. While stoichiometric H_2O_2 amounts promote the growth of oligomer chains adsorbed at the oxide surface, giving rise to highly porous, large surface area composites, an excess of H_2O_2 promotes homogenous phase reactions, leading to composites with higher PANI content and thermal stability, but more amorphous and with compact morphology. The composite properties can thus be tailored depending on the desired application. We tested the prepared composites towards the removal of wastewater pollutants, including both organic dyes and heavy metals. A fast and complete pollutant removal was achieved also in the presence of interferents. Consecutive tests with and without regeneration treatments showed promising results in terms of repeated usability, even in simulated drinking water matrix (Figure).

Pollutant removal tests: A) Cr(VI) consecutive reusage without regeneration treatments and B) repeated tests of dye removal and recovery



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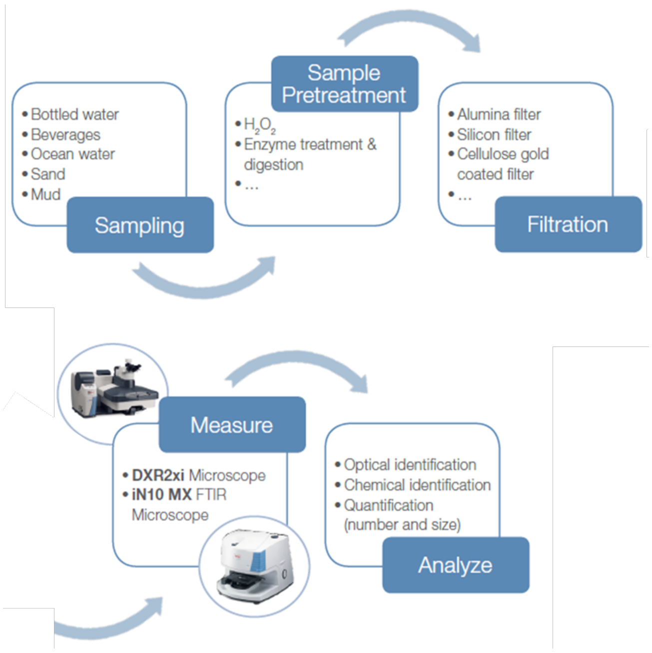
OC18

The fate of micro plastic in Earth environments. A proposed workflow for pollutant detection using Raman and Infrared micro-spectroscopy

Valerio Pasini, Barbara Bravo, Massimiliano Rocchia, Luigi Ciani
Thermo Fisher Scientific Spa, Strada Rivoltana, 20090, Rodano (MI), Italy
valerio.pasini@thermofisher.com

Abstract

Our use of plastics in everyday items and manufacturing processes has resulted in a deluge of slowly degradable materials entering our environment and our food chain. As plastics breakdown into tiny particles the consequences on human, animal and ecosystem health need to be studied. Hence, micro plastics, i.e. plastic particles less than 5 mm in diameter and down to few hundred of nanometers, are spread across the world, appearing everywhere, from the deepest sea trenches to Antarctica [1]. In addition, microplastics can carry variety of hazardous chemicals and plasticizer, such as bisphenol A (BPA), phthalates and persistent organic pollutants (POPs) which can affect animal and human health [2]. Raman and infrared microscopy can provide the proper identification of a wide range of microplastic particles (1-5000 μm diameter) collected from environmental, industrial, municipal or consumer-product samples. These techniques use the ability of light to interact with molecules causing them to vibrate at given frequencies. As a result, a spectrum (or a peak pattern of absorbed or emitted frequencies) can provide a "molecular fingerprint" of a microparticulate, providing the identity of its components. Here we will show how Infrared and Raman micro-spectroscopies are techniques capable of analyzing and quantifying specific individual particles, requiring easy sample preparation and providing information on each of them about size, shape and chemical composition.



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OC19

Incorporation of 2D black phosphorus (2D-bP) in polymer matrices for designing new materials with tuned morphological and spectroscopic features

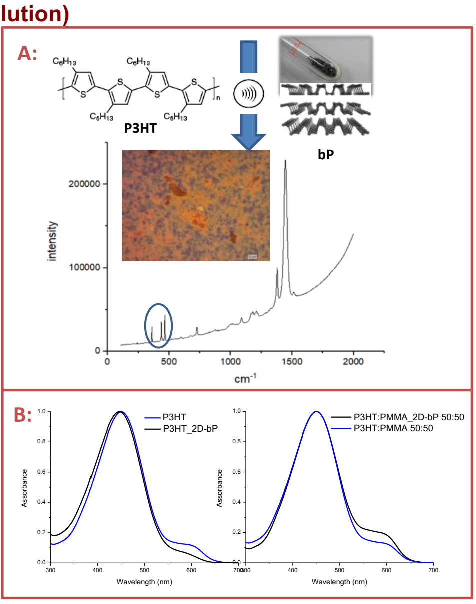
Elisa Passaglia,[a] Serena Coiai,[a] Francesca Cicogna,[a] Doriana Scittarelli,[a] Stefano Legnaioli,[a] Silvia Borsacchi,[a] Andrea Ienco,[b] Manuel Serrano-Ruiz,[b] Maria Caporali,[b] Maurizio Peruzzini,[b] Franco Dinelli,[c] Andrea Lazzeri,[d] Francesca Signori,[d] Randa Ishak[d]

[a] CNR-Institute for the Chemistry of OrganoMetallic Compounds, SS Pisa, via Moruzzi 1, 56124, Pisa, Italy
[b] CNR -Institute for the Chemistry of OrganoMetallic Compounds, via Madonna del Piano 10, Sesto Fiorentino (FI), 50019, Italy
[c] CNR- National Institute of Optics (CNR-INO), via Moruzzi 1, 56124, Pisa, Italy
[d] Department of Civil and Industrial Engineering, University of Pisa, largo L. Lazzarino 1, 56122, Pisa, Italy
elisa.passaglia@pi.iccom.cnr.it

Abstract

2D-bP (2D-black phosphorus or phosphorene) has recently gained considerable attention in the scientific community thanks to its peculiar electronic properties, which make it particularly attractive for designing devices for optoelectronics [1]. 2D-bP is generally produced from black phosphorus (bP) by mechanical exfoliation, a non-scalable procedure, or by liquid phase exfoliation (LPE). This latter methodology requires prolonged sonication in high-boiling dispersing solvents which must be removed before 2D-bP application. For this reason, LPE is not a simple and friendly technique. Furthermore, the intrinsic instability of 2D-bP in ambient conditions requires developing suitable procedures to protect the surface of the layers by covering them with organic and / or inorganic materials or by incorporating them in polymeric matrices. Recently, in our laboratory, a 2D-bP dispersion / stabilization methodology has been developed through an in situ polymerization process, where the monomer acts as a dispersing agent capable of intercalating the bP [2]. Therefore, the polymerization process provides a solid material in which the 2D-bP is intimately embedded into the polymer matrix and is protected against environmental degradation. With these composites it has already been possible to design micro-devices with electronic properties similar to those of 2D-bP provided by conventional mechanical exfoliation, with a simple procedure that avoids also the use of protecting atmosphere [3]. The mixing of the poly(methyl methacrylate) composites (PMMA_2D-bP) with a semiconductor polymer such as the regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) has been therefore carried out to study the effects of 2D-bP on the general properties of PMMA:P3HT mixtures, in order to evaluate their possible application in devices for optoelectronics. The results indicate that 2D-bP can be easily incorporated into PMMA, as well as into P3HT and PMMA:P3HT blends both through LPE and in situ polymerization approaches. Materials with a good dispersion and stability of 2D-bP, as proved by Raman and solid state ^{31}P-NMR have been obtained. In particular the collected composites have been characterized from structural, morphological and spectrophotometric point of view to evaluate the effects of 2D-bP on their ultimate properties in comparison with neat polymers (PMMA and P3HT) and blends (PMMA:P3HT). Interestingly, it has been observed that 2D-bP is located between the polymer chains of P3HT by maintaining excellent stability in the final composite and varying the UV response of the polymer with a significant reduction in the aggregation of macromolecules in solution and even in the solid state. This behavior suggests an effective interaction between the polymer and the 2D-bP and it can be reproduced or completely reversed in PMMA:P3HT mixtures. In fact separation of P3HT chains or their aggregation in PMMA:P3HT mixtures depends on whether the 2D-bP has been initially incorporated: into the P3HT or into the PMMA. Furthermore, the different displacement of 2D-bP causes a variation in the morphology of the blends as evaluated by SEM and AFM analysis carried out onto the surfaces of films obtained by spin-coating on Si/SiO$_2$ wafers. In particular co-continuous morphologies characteristic of PMMA:P3HT (50:50) mixture have been changed in a more phase-separated and globular arrangement suggesting a P3HT portion vertical phase segregation.

A: Schematic preparation procedure of P3HT_2D-bP composite, its optical image and its Raman spectrum; B: UV spectra of P3HT and P3HT:PMMA 50:50 and their related composites (CHCl$_3$ solution)



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Acknowledgments

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O20

Novel block copolymer nanocarriers for enhanced solubilization and sustained release of caffeic acid phenethyl ester

Petar D. Petrov,[a] Georgy Grancharov,[a] Mariya-Desislava Atanasova,[a] Krassimira Yoncheva,[b] Virginia Tzankova[b]

[a] Institute of Polymers, Bulgarian Academy of Sciences, Akad G. Bonchev st. 103A, 1113 Sofia, Bulgaria

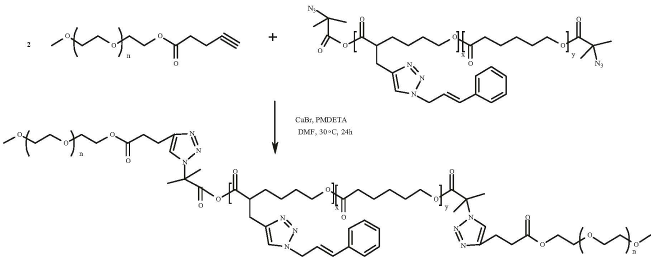
[b] Faculty of Pharmacy, Medical University of Sofia, 1000 Sofia, Bulgaria

ppetrov@polymer.bas.bg

Abstract

The natural bioactive substance caffeic acid phenethyl ester (CAPE) is well known for its anticancer, antiinflammatory, and antioxidant activity, among others. However, the poor solubility of CAPE in water significantly decreases its bioavailability and favorable biodistribution. The use of polymeric nanocarriers for improving the pharmacokinetic characteristics of CAPE-based formulations seems a promising approach. In this contribution, we report a strategy for enhancing the solubility of CAPE in water by novel block copolymer nanocarriers comprising segments structurally similar to the CAPE molecule. A series of amphiphilic poly(ethylene oxide)-b-poly(α-cinnamyl-ε-caprolactone-co-ε-caprolactone)-b-poly(ethylene oxide) (PEO-b-P(CyCL-co-CL)-b-PEO) triblock copolymers were synthesized by combining ring-opening copolymerization and "click" reactions. The calculations of the Flory–Huggins parameter suggested that P(CyCL-co-CL) copolymers have a higher affinity for CAPE than unmodified PCL homopolymer. Hence, micellar carriers based on PEO-b-P(CyCL-co-CL)-b-PEO were formed via the solvent evaporation method and then loaded with CAPE. Analyses by dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM) showed the formation of nanosized spherical micelles. A comparative study between PEO-b-P(CyCL-co-CL)-b-PEO and PEO-b-PCL-b-PEO systems revealed that the attachment of pendant cinnamyl moieties to the hydrophobic PCL block enhanced the encapsulation efficiency of the micelles and contributed for the sustained release of CAPE.

Synthesis of the PEO-b-P(CyCL-co-CL)-b-PEO) triblock copolymers by "click" reactionsof the PEO-C≡CH and N_3-P(CyCL-co-CL)-N_3 macroreagents



Acknowledgments
All the authors acknowledge financial support by the Bulgarian National Science Fund - Grant number DN 09-1/2016.

OC21

Self-structuring of main-chain and pH-dependent conformation of *L*-glutamine-based polyamidoamino acid: a molecular dynamics study

Giuseppina Raffaini,[a] Fabio Ganazzoli,[a] Federica Lazzari,[b] Amedea Manfredi,[b] Jenny Alongi,[b] Francesca Vasile,[b] Elisabetta Ranucci,[b] Paolo Ferruti[b]

[a] Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, via L. Mancinelli 7, 20131, Italy

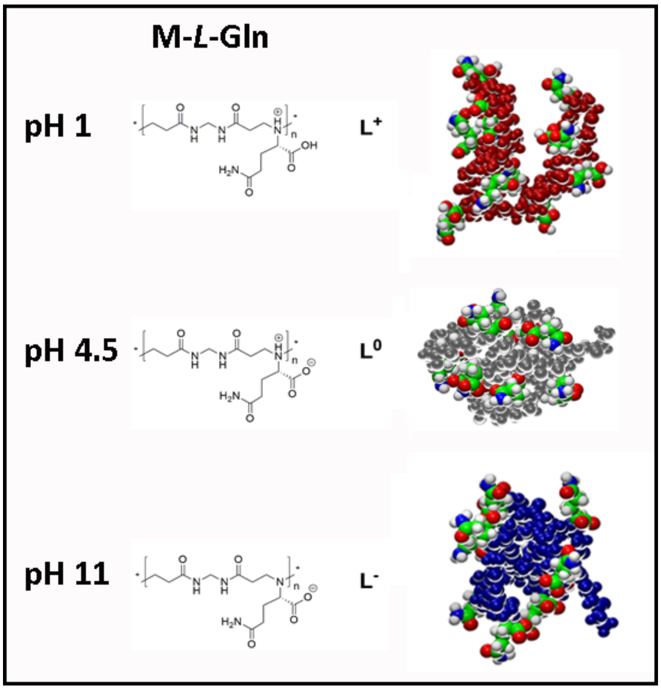
[b] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy

giuseppina.raffaini@polimi.it

Abstract

Many natural polymers spontaneously self-organize in water into stable and ordered conformations and often assemble into supramolecular structures thanks to non-covalent interactions. An interesting strategy is to design chiral synthetic polymers as new biomaterials in order to have synthetic biomaterials with performances close to that of natural ones [1,2]. Recently, a new chiral polymer family deriving from natural α-amino acids, polyamidoamino acids (PAACs), was obtained by polyaddition of *N,N′*-methylenebisacrylamide with natural amino acids [3,4]. Using Molecular Mechanics (MM) and Molecular Dynamics (MD) methods, adopting the same simulation protocol used in previous work [3,4], the conformational properties of *L*-glutamine-based polyamidoamino acid were studied. The theoretical results were compared with experimental data based on circular dichroism and NMR techniques and with the theoretical results previously obtained considering PAACs based on *L*-arginine and on hydrophobic aminoacids such as *L*-alanine, *L*-valine and *L*-leucine [3,4]. As in previous work, an interesting good agreement with experimental data was found, in particular about the dimension of PAAC M-*L*-Gln decamer considered at different pH (see Figure at right): the radius of gyration compared with hydrodynamic radius is very similar. The conformation at different pH displays a parallel disposition of main-chain strands topologically distant in a hairpin conformation, with a specific coiled structure at the isoelectric pH. This specific compact structure assumed at pH 4.5 is due to H-bonds among the main-chain and side-chain atoms. In this particular conformation the distance among H atoms in the optimized geometry found after MD run at room temperature and energy minimization in water, confirm the short distances among hydrogen atoms of main-chain and side chain groups topologically distant as found in NOESY experiments on M-*L*-Gln considering these specific atoms. Therefore, it is important to highlight this typical hairpin disposition of main-chain atoms of M-*L*-Gln decamer at different pH as found for previous PAAC polymers studied [3,4], confirming that these specific atoms in the PAACs main-chain greatly influence the dihedral angles distribution in a self-ordered structure. Once again, at acid pH the conformation is well swollen, decreasing the repulsion among positively charged nitrogen atoms of the protonated *tert*-amine atoms; at the isoelectric pH the structure is more compact, exposing glutamine side-chain on the molecular surface and optimizing all possible intramolecular H-bonds; at basic pH a compact structure exposing side-groups minimizing the repulsion among negatively charged side-chain atoms is observed. These polymers display a hairpin ordered conformation in the main-chain thanks to amide groups, typical bonds in polypeptides backbone without being themselves peptides. In addition, these polymers have α-amino acids in the side-chain, inducing different swollen or coiled structure enhancing the H-bonds when possible, in a pH-dependent conformation. PAACs are chiral synthetic polymers with very interesting potential use in biomaterials field.

Conformation of M-*L*-Gln decamer studied at different pH



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OC22

Development of novel furan-based polyester blends

Daniele Rigotti,[a] Andrea Dorigato,[a] Michelina Soccio,[b] Nadia Lotti[b]

[a] University of Trento, Department of Industrial Engineering, via Sommarive 9, 38123, Trento, Italy

[b] University of Bologna, Department of Civil, Chemical, Environmental and Materials Engineering, via Terracini 28, 40131, Bologna, Italy

rigotti.daniele-1@unitn.it

Abstract

The depletion of fossil resources and the growing environmental concerns have led to an increased interest in polymers from renewable resources. Furthermore, the use of renewable raw materials meets guidelines of green chemistry such as the establishment of convenient and less toxic materials. The replacement of petrochemical derivatives and the development of new materials can be achieved from the catalytic conversion of sugars to furan derivatives such as 2,5-furan dicarboxylic acid (FDCA) [1]. Polyesters based on FDCA show noticeable gas barrier, mechanical and thermal properties and are considered as the biobased alternatives to fossil-based terephthalate polyesters (PET), which are one of the most diffused polymers on the market, with a production of more than 50 megatons per year [2]. Moreover, legislation in Europe and USA is currently favoring the use of "green" materials, enhancing them against oil-based products. Many scientific studies are focused on FDCA, due to the wide variety of materials that can be produced from this precursor. FDCA based polymers are thus valuable alternatives to oil-based products. In some cases, biobased polymeric products have superior properties compared to oil-based products [2]. Poly(lactic acid) (PLA) has become nowadays the most used biodegradable material produced from completely renewable sources, such as corn, sugar, and vegetables. This material is characterized by excellent mechanical properties, which are comparable to those of other conventional polymers produced from petroleum sources, and good processability. However, its brittleness and the rather low barrier properties limit the range of application of this polymer [3]. In the present work the production and the characterization of novel polymer blends materials, composed of poly(pentylfuranoate) (PPeF) and polylactic acid (PLA), is reported. The preparation of blends into thin films for the development of tougher PLA based materials for packaging applications was presented and discussed. The attention was focused on their mechanical, morphological and barrier properties, which are fundamental features for the design on new biobased plastics for packaging applications. Moreover, also the preparation of fibers starting from blended materials through a solvent spinning process is reported. The process parameters were optimized and the thermo-mechanical behavior of the resulting fibers was investigated.

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OC23

See what is really happening within your furnaces

Olivier Savard,[a] Masaaki Muraoka[b]

[a] Hitachi High-Tech Analytical Science Ltd., Windrush Court, Abingdon Business Park, Abingdon, OX14 1SY UK

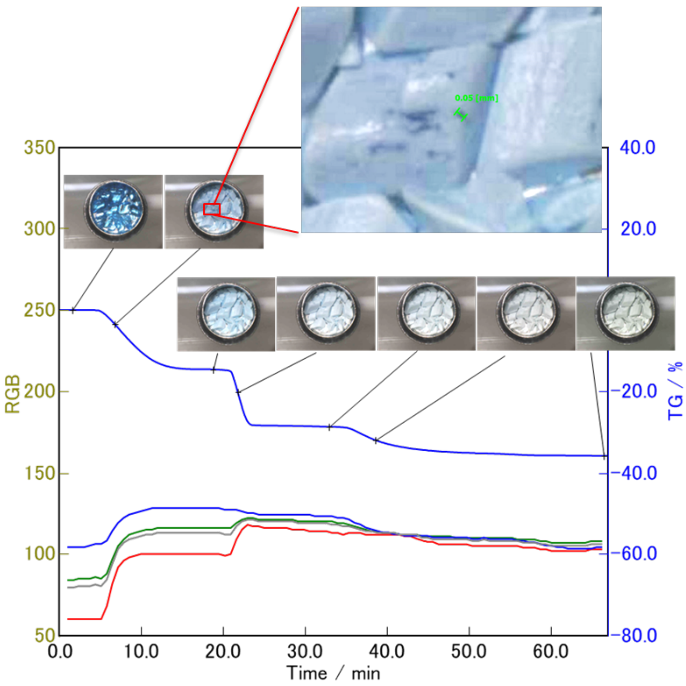
[b] HITACHI HIGH-TECH SCIENCE CORPORATION, 24-14, Nishi-Shimbashi 1-chome, Minato-ku, Tokyo 105-0003, Japan

olivier.savard.os@hitachi-hightech.com

Abstract

Although thermal analysis techniques like DSC, STA, DMA and TMA have been around for a long time, it's always been a challenge to know what is really happening to our samples during an experiment. From colour to dimension changes, being able to see how the sample behaves when heated up or cooled down can add important information to the thermal analysis story. Visible images can also be used as a valuable troubleshooting tool to explain an unusual behaviour during an experiment. This presentation will go through the advantages of being able to see the samples while using thermal analysis techniques (DSC, STA, DMA and TMA). Real examples will be used to show the power of the techniques and it will also cover the extra information which can be extracted from a visible image (e.g. RGB values).

Real View® Example with RGB Values



Acknowledgments

A special thanks to the HITACHI HIGH-TECH SCIENCE CORPORATION application team at Hitachi Shimtomi Lab in Tokyo.

OC24

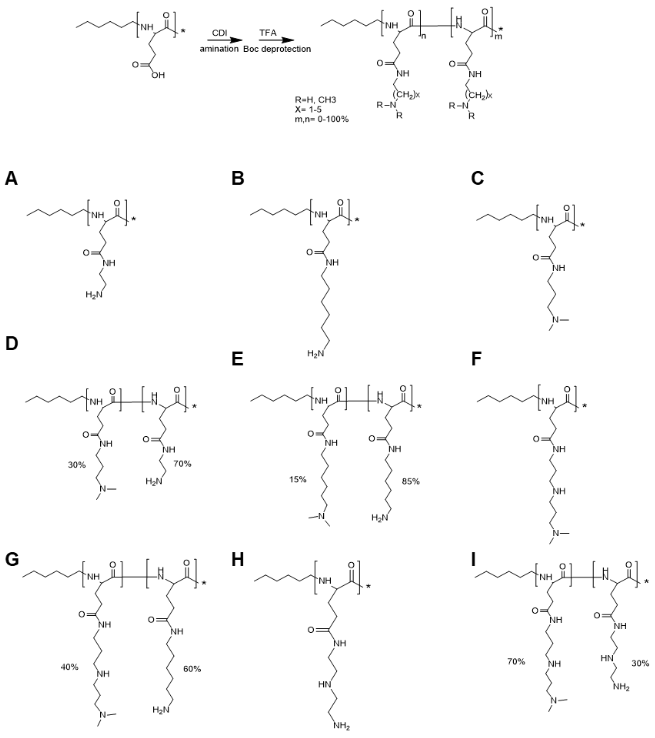
Aminated poly(α)glutamate for the systemic delivery of siRNA to solid tumors

Anna Scomparin,[a,b] Adva Krivitsky,[b] Dina Polyak,[b] Shay Eliyahu,[b] Ronit Satchi-Fainaro[b]
[a] Department of Drug Science and Technology, University of Turin, Via P. Giuria 9, Torino, 10125, Italy
[b] Department of Physiology and Pharmacology, Sackler Faculty of Medicine, Room 607, Tel Aviv University, Tel Aviv 69978, Israel
anna.scomparin@unito.it

Abstract

The discovery of RNA interference (RNAi) and the recognition of the ability of oligonucleotides to target "undruggable" oncogenic pathways, rendered clear the need of an adequate carrier suitable for the *in vivo* administration of the therapeutic nucleotides. Such a delivery system not only must prevent the degradation during circulation, but also should promote site-specific uptake. To date, most of the developed systems failed to accomplish this task, including the few oligonucleotide-based nanomedicines that reached clinical trials [1]. To overcome this limitation, a library of novel nanocarriers based on aminated poly(α)glutamate have been designed, synthesized, and physico-chemically characterized [2]. The polymers differ for the length and structure of the side-chain amine moiety. All the synthesized biodegradable polymers were able to complex oligonucleotides forming nano-sized polyplexes, but each one was able to internalize into cells and cause silencing at a different extent. The structures modified with linear alkyl chain that terminates by primary amine **(polymer A, B)** or linear alkyl chain that terminates by tertiary amine and bears secondary amine **(Polymer F, I)** displayed the higher silencing activity. We further investigated the effect of introducing alkyl side-chains on the polymeric backbone, synthesizing an amphiphilic alkylated poly(α)glutamate amine (APA) [3]. APA:siRNA polyplexes were shown to be potent gene regulators *in vitro*, but failed to induce specific mRNA degradation *in vivo*. Among all the developed polyplexes, the treatment with PGAamine-Rac1 siRNA polyplex (siRac1-polyplex) **(Polymer A)** caused specific gene silencing by 80% in HeLa and SKOV-3 human ovarian adenocarcinoma cells as opposed to PGAamine-control non-targeting siRNA polyplex (siCtrl-polyplex) leading to inhibition of cell migration and wound healing abilities. Following intraperitoneal administration of siRac1-polyplex to mCherry-labeled ovarian adenocarcinoma-bearing mice, the polyplexes accumulates at the tumor site, with 38% Rac1 knockdown. The systemic treatment of SKOV-3 tumor-bearing mice with siPlk1-polyplex inhibited tumor growth by 73% and 87% compared with siCtrl-polyplex or saline-treated mice, respectively, leading to prolonged overall survival [4]. These findings represent the first time that a polyaminated poly(α)glutamate polymer is used for an efficacious and safe tumor delivery of RNAi following systemic administration.

Synthetic mechanism and chemical structure of Aminated poly(α)glutamate



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OC25

Novel linear amphiphilic polyglycidol/poly(ε-caprolactone) copolymers prepared via “click” chemistry-based reactions

Natalia Toncheva-Moncheva,[a] Pavel Bakardzhiev,[a] Stanislav Rangelov,[a] Barbara Trzebicka,[b] Aleksander Forys,[b] Petar D. Petrov[a]

[a] Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St. 103A, 1113 Sofia, Bulgaria

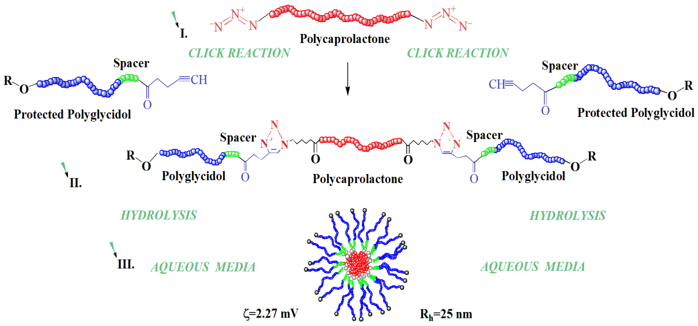
[b] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Sklodowskiej 34, 41-819 Zabrze, Poland

ntoncheva@polymer.bas.bg

Abstract

The “click” chemistry concept was successfully applied for the preparation of amphiphilic block copolymers comprising linear polyglycidol (PG) and poly(ε-caprolactone) (PCL). This new class of linear amphiphilic block copolymers of precisely designed macromolecular characteristics and predefined composition were synthesized to demonstrate the convenience of this strategy as compared to the classical approaches of sequential ROP. Monohydroxyl poly(ethoxyethylglycidyl ether) (PEEGE) precursors were synthesized by ring-opening anionic polymerization of ethoxyethylglycidyl ether (EEGE) and subsequently functionalized with a “clickable” alkyne end group. In parallel, a bifunctional PCL diol was modified to an azide-terminated macroreagent. PG/PCL block copolymers were obtained via cooper catalyzed cycloaddition reaction of the as prepared alkyne- and azide-functional macroreagents and subsequent cleavage of the protective ethoxyethyl groups of PEEGE. The amphiphilic block copolymers were not directly soluble in water, and defined nano-sized micelles with slightly positive ζ potential were obtained via the solvent evaporation method. We anticipate a core–shell structure comprising a biodegradable hydrophobic PCL core and a functional hydrated PG shell. The small size in combination with the favorable physicochemical properties of the building blocks makes the micelles a promising platform for multifunctional nanocarrier development. Moreover, the synthesis pathway described here can be extended toward synthesis of various functional block copolymers comprising linear PG.

Synthesis of Polyglycidol/Poly(ε-caprolactone) linear copolymers



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OC26

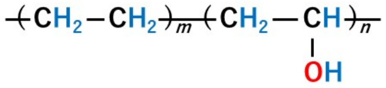
Innovative & sustainable high barrier solutions for circular economy

Tomonori Yoshida
Mitsubishi Chemical Performance Polymers (MCPP™), Merowingerplatz 1A, Düsseldorf, 40225, Germany
Tomonori.Yoshida@mcpp-europe.com

Abstract

Contribution to circular economy is one of the most important tasks for plastic industry. Global production of plastics is 348 million tons in 2018, which expected to double over the next 20 years, and over 25 million tons per year of plastic waste are generated in Europe. Less than 30% of such waste is collected for recycling, but the rest is going to landfill or leaks to environment. 95% of the value of plastic packaging material is lost to the economy after a very short first-use cycle. Globally, 5 to 13 million tons of plastics (1.5 – 4% of global plastics production) end up in the oceans every year [1]. Nippon Gohsei Europe, a group company of Mitsubishi Chemical cooperation, offers several innovative solutions to contribute circular economy. Soarnol™, ethylene vinyl alcohol *co*-polymer (EVOH, Fig. 1), is a recyclable high gas barrier plastic and is widely used as a barrier layer of multilayer food packaging to reduce the packaging and food waste by prolonging the shelf life. The packaging with EVOH and polyolefin can be recyclable which contributes further reduction of the plastic waste. Soaresin™ RG500, a compatibilizer of EVOH with polyolefin, improves recyclability of EVOH to enhance the flexibility of the packaging design. A typical example of internal EVOH/polyolefin recycling is described in Fig. 2. Furthermore, a Mitsubishi chemical's newly developed high clarity EVOH widens processability for superior appearance and better mechanical properties on multilayer packaging by improving surface roughness between EVOH and tie layer (Fig. 3). Transparency is one of the important properties for food packaging and polyamide is normally used in between EVOH and tie layer to improve the transparency by decreasing interface instability. However, polyamide is more difficult to recycle with polyolefins duo to a big difference in processing temperatures and viscosity. High clarity EVOH offers polyamide free structure for easy recycling. Nichigo G-Polymer™, a modified polyvinyl alcohol, is a biodegradable, water-soluble and high gas barrier plastic (Fig. 4). It gives innovative solutions. Total biodegradable high gas barrier packaging can be offered as one solution for plastic waste management with the combination of other biodegradable plastics like PLA or PBS. Moreover, Nichigo G-Polymer™ can offer "wash-away technology" for easy recycling. Since Nichigo G-Polymer™ has excellent water solubility, even if it is in a multilayer packaging, Nichigo G-Polymer™ can easily dissolve into water to isolate base plastics (polyolefin, PET, PS, etc) as mono-material, which improves recyclability of plastic waste dramatically. An example of the Separation-Technology is described in Fig. 5. Nippon Gohsei Europe and Mitsubishi chemical cooperation create innovative solutions globally based on our core values of sustainability, health and comfort, striving for the well-being of people, society and our planet Earth.

Figure 1. Structure of Soarnol™ (EVOH)



$$\left(CH_2-CH_2\right)_m\left(CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}\right)_n$$

Figure 2. Example of EVOH/PO recycling

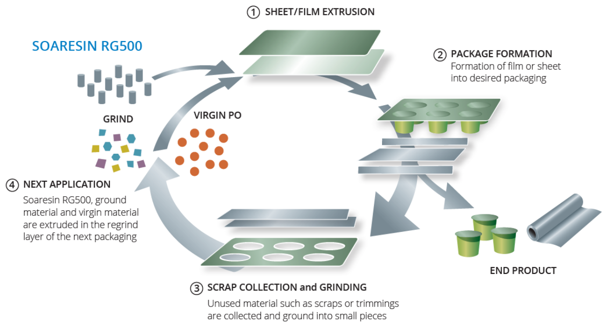


Figure 3. Effect of intersurface instability to film appearance

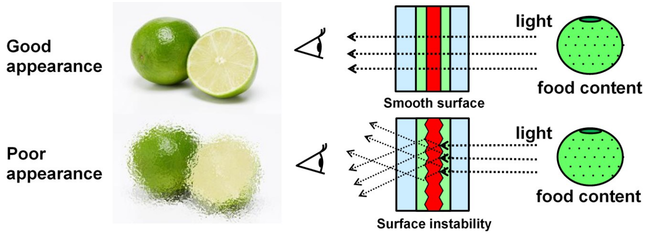


Figure 4. Structure of Nichigo G-Polymer™

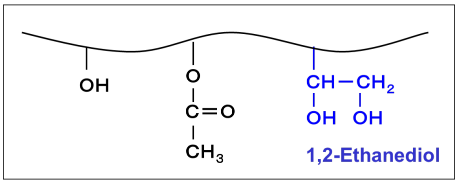
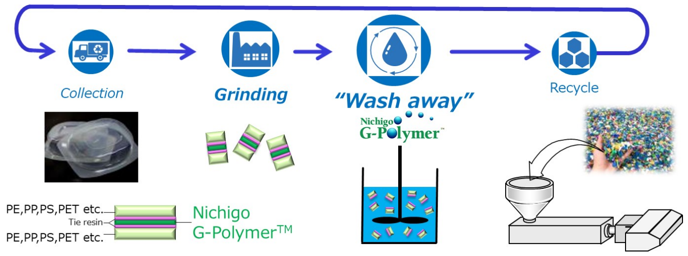


Figure 5. Separation-Technology with Nichigo G-Polymer™



References

1. Source from EPEA Internationale Umweltforschung GmbH.

OC27

Ultrasonication-mediated atom transfer radical polymerization in miniemulsion for the preparation of precisely-defined complex polymer architectures

Izabela Zaborniak, Paweł Chmielarz

Department of Physical Chemistry, Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

i.zaborniak@stud.prz.edu.pl

Abstract

Due to the increasing requirement for more environmentally and industrially relevant approaches in the synthesis of functional polymeric materials, ongoing developments and improvements of reversible-deactivation radical polymerization (RDRP) techniques, especially atom transfer polymerization (ATRP) going through reducing or completely eliminating of chemical reagents and solvents from reaction setup. In this contribution, the headline aim of our research is the implementation of ultrasound-mediated ATRP (sono-ATRP) to miniemulsion media [1]. Among the other ATRP approaches, sono-ATRP eliminates a necessity of using an additional chemical compound as a reducing agent and in the context of environmentally friendly approaches which apply external stimuli - enables control of the polymerization rate by switching ultrasonication on/off but uses a simple and easy to scale-up reaction setup, while resulting in excellent control during polymerization receiving macromolecules with high MW and narrow MWD [2,3]. Additionally, this solution is characterized by replacing organic by heterogeneous media characterized by low toxicity, low viscosity and also good heat transfer taking advantage in industrial application, especially in the context of biomedical and pharmaceutical application [4,5]. In the miniemulsion system the catalysis is described by two principal mechanisms -interfacial and ion-pair catalysis (Figure 1). As a result of ultrasonication catalyst complex is reduced at the surface of monomer droplets (95% of the catalyst) [6] initiating the polymerization in accordance with interfacial catalysis and on the other hand is subsequently combined with sodium dodecyl sulfate (SDS) acts as an anionic surfactant, results in formation of neutral ion pairs, Br-Cu^{II}TPMA$^+$/DS$^-$, that possess ability to activate polymer inside of BA droplets (1% of catalyst) [6] reflecting interfacial catalysis. A residual amount of catalytic complex (4%) [6] remains in the aqueous phase.

In the beginning, this novel approach was successfully applied to the synthesis of homo- and copolymers using a wide range of monomers, both acrylates and methacrylates. The results indicate a control characteristic of polymerization processes proved by liner kinetics and narrow molecular weight distribution (MWD) of received macromolecules. Temporal control over the polymer chain growth was successfully conducted by turning the ultrasonication on/off. The synthesis was efficiently reinitiated without any influence on controlled characteristic maintaining the precise structure of received homopolymers [1]. Going a step further, sono-ATRP in miniemulsion was used to polymerize acrylates from naturally-derived macroinitiator based on sucrose and lactulose structure. Prepared star-shaped polymers with sugars-based core and acrylate arms were characterized by a precisely-controlled structure indicates by low dispersity of both star-like polymers and cleaved arms. This procedure constitutes an excellent, simple and eco-friendly approach in the preparation of functional polymeric materials based on linear and complex structures.

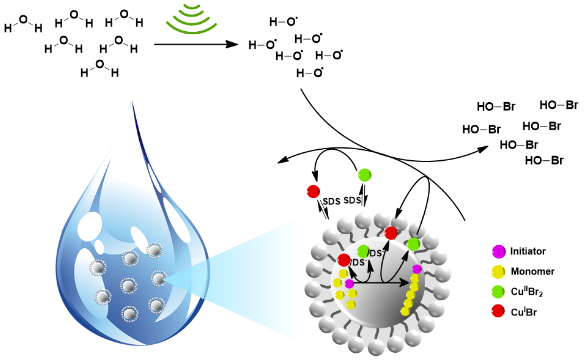


Figure 1. Ultrasound-mediated atom transfer radical polymerization (sono-ATRP) in miniemulsion [1]

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POSTER COMMUNICATIONS

P1

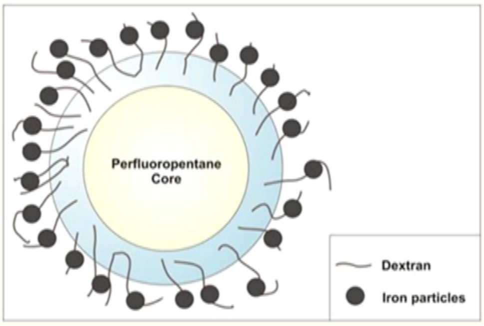
Spion decorated oxygen-loaded nanobubbles as theranostic hyperthermic agent for tumor oxygenation

Shoeb Ansari,[a,b] Monica Argenziano,[b] Federica Albertini,[c] Caterina Guiot,[a] Roberta Cavalli[b]
[a] Department of Neurosciences, University of Torino, via Cherasco 15, 10126, Torino, Italy
[b] Department of Drug Science and Technology, University of Torino, via P. Giuria 9, 10125, Torino, Italy
[c] Consiglio Nazionale delle Ricerche, Istituto dei Materiali per l'Elettronica ed il Magnetismo, Parco Area delle Scienze 37/A, 43124, Parma, Italy
shoebanwarmohammedkhawja.ansari@unito.it

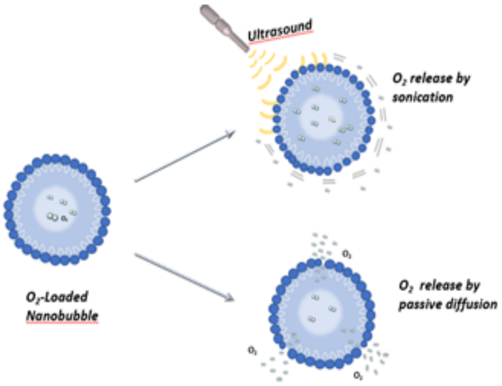
Abstract

Tumor hypoxia is associated with resistance to radiotherapy. The combination of hyperthermia and radiotherapy have been proposed to enhance tumor radiosensitivity [1]. Moreover, the tumor oxygenation through local oxygen delivery can improve the therapeutic outcomes also in cancer chemio-treatment. The aim of this work was the development of superparamagnetic oxygen-loaded nanobubbles (MOLNBs) as an innovative nanoplatform able to combine hyperthermic treatment with direct tumor oxygenation. Nanobubbles (NBs), spherical core-shell structures, have been proposed as multifunctional theranostic agent with the capability to provide ultrasound (US) imaging and drug delivery [2,3]. Dextran shelled and perfluoropentane cored nanobubbles were prepared, loaded with oxygen and functionalized Superparamagnetic Iron Oxide Nanoparticles (SPIONs). The NB formulations were *in vitro* characterized evaluating the Physico-chemical parameters, the morphology, the in vitro oxygen release kinetics and the physical stability over time. Moreover, hyperthermic and magnetic measurements were carried out and the NB echogenicity was evaluated by ultrasound imaging. NBs with size of about 350 nm and negative surface charge, able to bind SPIONs by electrostatic interactions were obtained. They were able to store oxygen and release it in Saline solution with prolonged kinetics. *In vitro* investigation showed that magnetic NB formulation can produce temperature increase when exposed to Radiofrequency magnetic fields. The ability of NBs to generate an echogenic response was demonstrated by B-mode US imaging. Finally, SPION decorated oxygen-loaded nanobubbles might represent a theranostic nanotool for multimodal tumor treatment, both inducing hyperthermia upon radio-frequency (RF) magnetic field exposure and releasing oxygen as radio-sensitizer for radiotherapy.

Oxygen loaded NBs (OLNBs) COATED WITH SPIONs = MOLNBs



Oxygen release



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P2

Polymer-shelled nanobubble formulation to hamper hypoxic pancreatic cancer

Federica Bessone,[a,b] Shoeb Ansari,[c] Anna Scomparin,[a] Enrico Giraudo,[a,b] Roberta Cavalli[a]

[a] Department of Drug Science and Technology, University of Turin, via P. Giuria 9, 10125, Torino, Italy

[b] Laboratory of Tumor microenvironment, Candiolo Cancer Institute - FPO, IRCCS, Strada Provinciale 142, Km 3.95, 10060, Candiolo (TO), Italy

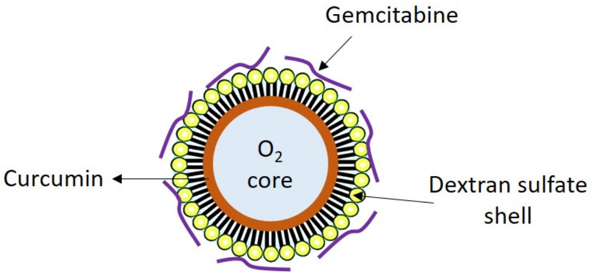
[c] Department of Neurosciences, University of Torino, via Cherasco 15, 10126, Torino, Italy

f.bessone@unito.it

Abstract

Hypoxic tumors are generally more resistant to chemotherapy and radiation. In particular, pancreatic cancer is an aggressive type of malignancy in which the microenviroment (TME) is extremely hypoxic, contributing to the drug resistance. The TME is characterized by fibrosis separating tumor cells from blood vessels, extensive desmoplasia (abundant and dense collagenous stroma) and depletion of oxygen. In response to decreased oxygen levels, due to the low perfusion caused by aberrant vasculatures, pancreatic cancer cells try to adapt to the condition of TME and activate hypoxia-inducible factors (HIFs) [1]. In particular, HIF-1α plays an important role in inducing the expression of different factors involved in cancer progression, promoting extracellular matrix remodeling, abnormal angiogenesis, cell migration, metastasis, and drug resistance [2]. Notably, the prevalent mechanism for chemotherapy resistance is an increased expression of efflux transporters that pump out the anticancer drugs from the cells. The main class of drug efflux pumps is the ATP-dependent binding cassette (ABC) transporter superfamily and in particular the multi-drug resistant protein-1 (MDR1). With the purpose to address multiple aspects in the fight of pancreatic cancer, novel polymer-shelled nanobubble (NB) formulations were developed. The NBs were designed with the aim to supply oxygen, anticancer drugs and adjuvant agents to the pancreatic tumor site. Different NB formulations were prepared, combining: i) oxygen with the attempt to revert the hypoxic TME; ii) gemcitabine as chemotherapeutic drug to block cancer cell growth; iii) curcumin as an inhibitor of overexpressed MDR1 in resistant cancer cells. Oxygen/Gemcitabine/Curcumin-loaded nanobubbles (GS-Oxy-NBs) were prepared and physicochemical characterized by measuring size, polydispersity index and surface charge. In these nanobubbles the oxygen is dissolved in the perfluoropentane core, the curcumin is loaded at the interface between the core and the shell, and the gemcitabine is electrostatically bounded to the dextran sulfate polymeric shell. The co-formulation was tested in vitro by evaluating the stability and the release kinetics of the different active agents. Moreover, the biological effect of GS-Oxy-NBs on murine pancreatic cancer cells (mPDAC) was assessed through an in vitro cytotoxicity assay. In addition, invasiveness of the PDAC cells, both in 2D and 3D cultures, was measured upon treatment with GS-Oxy-NBs. Finally, PDAC cells were treated, under normoxic or hypoxic (1% O_2) conditions, with Oxygen-loaded NBs (Oxy-NBs) to ensure the role of oxygen in restoring normoxya. Real Time RT-PCR analysis was conducted in order to evaluate the expression of the genes directly or indirectly regulated by HIF1-α. The synergistic effect of GS-Oxy-NBs may represent an interesting platform to overcome current drawbacks with the present treatment of pancreatic cancer.

Schematic representation of GS-Oxy-NBs



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P3

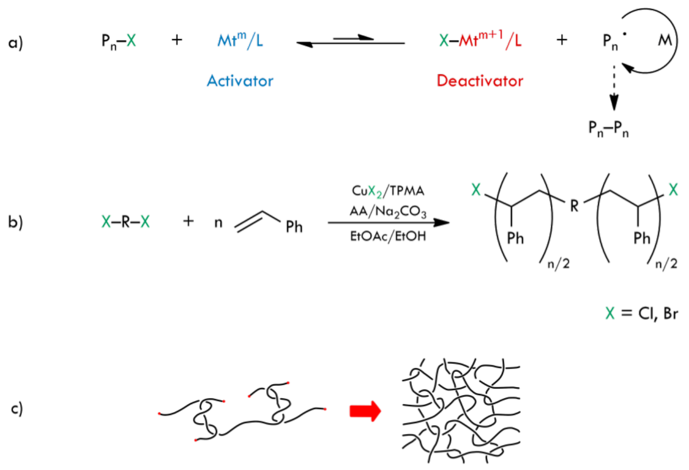
Anomalous gelation during the ARGET ATRP of styrene

Mirko Buffagni,[a] Niccolò Braidi,[a] Francesca Parenti,[a] Aldo Longo,[b] Angelo Ferrando,[b] Franco Ghelfi[a]
[a] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, via G. Campi 103, 41125, Modena, Italy
[b] Centro Ricerche "Claudio Buonerba", Versalis (Eni) S.p.A., via G. Taliercio 14, 46100, Mantova, Italy
mirko.buffagni@unimore.it

Abstract

Atom transfer radical polymerization (ATRP) is a type of reversible-deactivation radical polymerization, first described in 1995 [1,2]. ATRP allows the synthesis of polymers with low dispersities ($Đ < 1.1$) and the preparation of controlled molecular architectures, giving birth to new advanced materials. As highlighted in Figure a, ATRP is controlled by an equilibrium between halogenated dormant species (P_n–X) and propagating radicals ($P_n\cdot$). The dormant species periodically react with transition metal complexes in their lower oxidation state (Mt^m/L) to form the propagating radicals. In their turn, the propagating radicals can be deactivated by reaction with the transition metal complexes in their higher oxidation state ($X–Mt^{m+1}/L$). The ATRP control is assured by keeping the equilibrium toward the left and consequently the radical concentration low, avoiding termination reactions (dashed arrow). A type of activators regenerated by electron transfer (ARGET) ATRP process was developed by our group (Figure b). ARGET systems exploit a chemical reducing agent to generate the activator *in situ* from the deactivator [3]. In our system, the reducing agent is ascorbic acid (AA) and Na_2CO_3 is added to activate AA and to counteract the acidity. The bifunctional initiator (X–R–X) generates a polymer with two halogenated chain ends. The monomer is styrene, the transition metal is copper and the ligand is tris(2-pyridylmethyl)amine (TPMA). Lastly, the solvent is a mixture of ethyl acetate (EtOAc) and ethanol (EtOH). In specific conditions of reagents concentration and temperature, the reaction system evolved to a jelly-like consistency, without the addition of any crosslinker or gelling agent. The surprising discovery was patented [4]. The gelation could be reasonably explained with chain transfer processes or with the formation of new double bonds *via* dehydrohalogenation of the initiator or the polymer chain end, which can both give crosslinks and then gelation after termination reactions. However, these hypotheses were disproved by various scientific evidence, including the gelation of deuterated styrene and ^1H NMR spectra. At this time, the only plausible explanation for the phenomenon is the formation of an olympic network, a mechanically-interlocked architecture composed of interpenetrated macrocyclic polymer chains (Figure c).

a) ATRP equilibrium. b) The ARGET ATRP system we developed. c) Formation of an olympic network



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P4

Synthesis of polylactide matrix composites by resin transfer molding

Bernard Campos,[a] Elodie Louisy,[a,b] Fabienne Samyn,[a] Serge Bourbigot,[a] Gaëlle Fontaine,[a] Fanny Bonnet[a]

[a] Unité Matériaux Et Transformation, CNRS, UMR 8207, Villeneuve d'Ascq, France

[b] Unité de Catalyse et de Chimie du Solide, CNRS, UMR 8181, Villeneuve d'Ascq, France

bernard.camposm@gmail.com

Abstract

Composite materials exhibit many advantages over traditional materials and particularly in terms of lightness, mechanical resistance or chemical resistance [1]. The development of composites meets the requirements of industrial markets for applications in the fields of transport, construction, sports and leisure. In a context of sustainable development, a growing number of studies focus on the development of composites with biobased matrices [2]. Thus, polylactide (PLA) has become a major actor and could in the long term become an alternative to petroleum-based polyolefins [3].

Regarding the processes of composite manufacture, Resin Transfer Molding (RTM) is an innovative process based on the injection, in a mold containing fibers, of a monomer and a catalyst in order to carry out *in-situ* the polymerization of the matrix [4]. The major advantage over conventional melt processes is the access to high fiber content while improving their wetting by the matrix. Although a wide range of thermosetting matrix resins is available on the market, there are only few commercial resins for thermoplastic matrices. Regarding academic studies, composites based on poly(ε-caprolactone), were prepared [5,6], but no example was reported to date with lactide monomer.

In order to design PLA-based composites by RTM, tin octoate was chosen as the catalyst as it displays some of the higest activity for the polymerization of lactide [7]. Polymerization tests were first tested at the lab scale before being upscaled in the RTM process. Poly(L-lactide) (PLLA)-based composites with glass fibers as reinforcement were obtained (Figure 1) [8]. The resulting PLLA matrix exhibits conversions up to 98 % along with high molar masses of up to 78,000 g.mol-1, when the polymerization is carried out under dynamic vacuum, with a good impregnation of the fibers by the matrix (Figure 2).

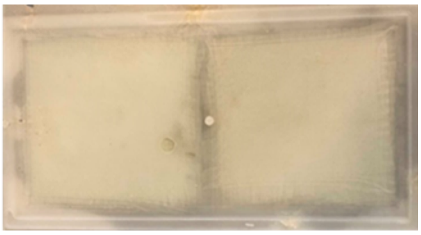

Figure 1. PLLA / glass fiber composite

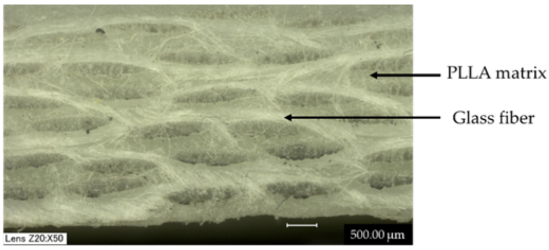

Figure 2. Optical microscopy picture of the composite

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P5

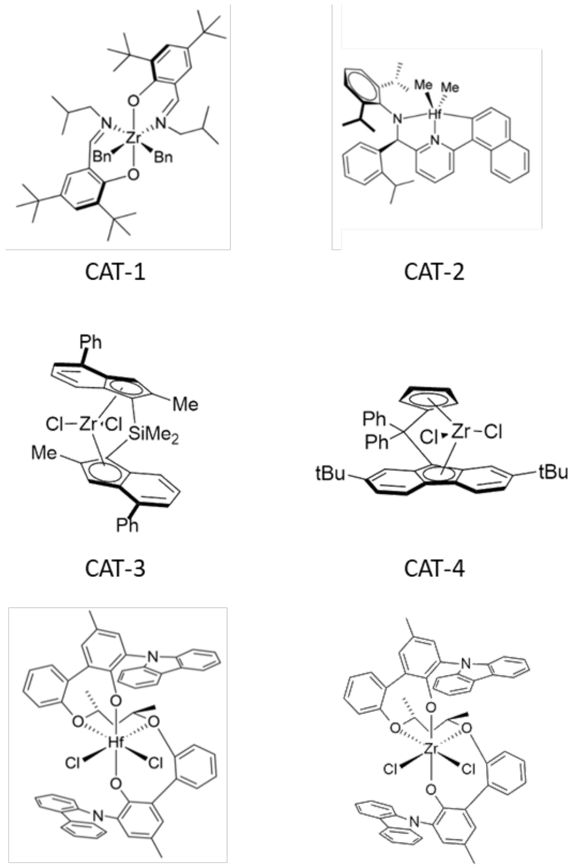
A high throughput experimentation (HTE) approach to coordinative chain transfer polymerization

Felicia Daniela Cannavacciuolo, Antonio Vittoria, Roberta Cipullo, Vincenzo Busico
Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Strada Vicinale Cupa Cintia 21, 80126, Napoli, Italy
feliciadaniela.cannavacciuolo@unina.it

Abstract

Coordinative Chain Transfer Polymerization (CCTP) and Chain Shuttling Polymerization (CSP) are innovative catalytic processes aimed to produce statistical olefin block copolymers [1,2], which represent the most advanced frontier of the polyolefin market and bear great promise for applications in a Circular Economy (e.g., compatibilizers for mechanical recycling). Whereas the only products that have reached the market are due to Dow Chemical (Infuse™ and Intune™ technologies) [3,4], in the literature a variety of metallocene and 'post-metallocene' catalysts, in combination with several main group metal alkyls, have been claimed as amenable to such processes [5]. In many cases, though, the claims are poorly based, due to an inadequate polymer characterization and/or exploration of the catalyst and process variable space. Demonstrating unambiguously the occurrence of CCTP or CSP is not trivial. As a matter of fact, the polymerization conditions are harsh (high temperature to allow for polymer chain mobility, concentrated metal alkyl species in solution), and the discrimination between physical and chemical polymer blends is often more complicated than one might think. Moreover, unraveling the molecular kinetics is very difficult, because the number of chemical and physical variables to consider is huge, and cross-interactions in the catalyst formulation are the norm. In our laboratory, an integrated state-of-the-art High Throughput Experimentation (HTE) workflow for the exploration of catalytic olefin polymerizations is operated. Protocols were successfully implemented to investigate CCTP and CSP rapidly and thoroughly. In this presentation, results will be shown for a variety of catalysts that, according to the literature, mediate olefin CCTP or CSP, starting with the catalyst pair (CAT-1, CAT-2) originally disclosed by Dow Chemical (Infuse™ technology). Unambiguous methods will be introduced to demonstrate CCTP; by applying such methods, it was concluded that well-working catalysts for olefin CCTP are extremely rare, and several literature claims (e.g., the case of CAT-3 and CAT-4) are actually flawed [6]. Last but not least, whether or not CCTP is achieved depends on subtle details of the catalyst formulation (CAT-5 and CAT-6 will be used as exemplifications in this respect).

The structures of the precatalysts screened in CCTP process



CAT-1 CAT-2

CAT-3 CAT-4

CAT-5 CAT-6

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P6

PEEK as a bone implant material modified *via* ATRP – aims, challenges and future perspectives

Monika Flejszar,[a] Paweł Chmielarz,[a] Michael Gießl,[b] Helmut Cölfen[b]

[a] Department of Physical Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

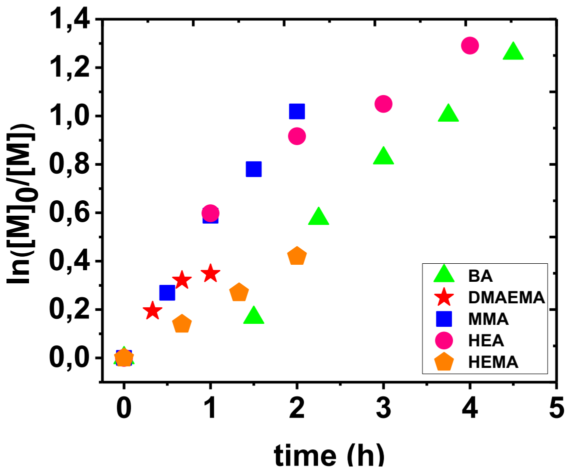
[b] University of Konstanz, Chemical Department, Universitaetsstraße 10, 78457 Konstanz, Germany

m_flejszar@stud.prz.edu.pl

Abstract

The spine, due to its functions in the body, is an essential organ for the proper functioning of humans. Although it is well protected by muscle and fat tissue, it is often damaged (both by natural factors and random events). Restoring the efficiency of the organ is often the life and death of a person. There are many surgical techniques that can contribute to this to a greater or lesser extent, but in recent years a new group of surgical tools has emerged that improve the treatment process and give hope for recovery for patients. These are implants for the treatment of back disorders. The first application of the poly(aryletheretherketone) (PEEK™) materials took place in 1990 when AcroMed from Cleveland introduced to the market copper rod ends made of poly(aryletherketone) (PAEK) [1]. Quickly commercial success encouraged researchers to chemical modifications this hydrophobic, biological inert and no toxic polymers making it a great candidate for various biological applications [2-4]. One of the new, unspecified possibilities of poly(ethyletherketone) PEEK modification is chemical surface modification *via* surface-initiated atom transfer radical polymerization (SI-ATRP). The advantage of grafting of polymer brushes over other surface modification methods is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility enabling the introduction of a variety of functional groups [5]. For this reason, five different types of well-defined polymer brushes were grafted from surfaces of PEEK *via* surface-initiated supplemental activator and reducing agent atom transfer radical polymerization (SI-SARA ATRP), by using $Cu^{II}Br_2$/TPMA as a catalyst. It was confirmed that both the molecular weight of resulting polymer increases linearly with increasing monomer conversion as well as the value of $\ln([M]_0/[M])$ as a function of polymerization time increases linearly. Due to the potential application, the studies are aimed at grafting biocompatible polymers like poly(dimethylaminoethyl methacrylate) (PDMAEMA) and poly(2-hydroxyethyl acrylate) (PHEA) brushes [6,7]. Moreover, the results of the grafting of three new types of polymeric brushes containing phosphorus will be presented. The presence of this element might be crucial to obtain material that will be easily biomineralized and accepted by the human body resulting in a material with high application potential.

First-order kinetic plots for polymer brushes grafted from PEEK surface



**BA- buthyl acrylate; DMAEMA - dimethylaminoethyl methacrylate; MMA – methyl methacrylate; HEA - 2-hydroxyethyl acrylate; HEMA – methyl methacrylate*

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P7

Multifunctional polyurethane foams with thermal energy storage/release capability

Francesco Galvagnini,[a] Andrea Dorigato,[a] Francesco Valentini,[a] Vincenzo Fiore,[b] Maria La Gennusa,[b] Alessandro Pegoretti[a]

[a] University of Trento, Department of Industrial Engineering and INSTM Research Unit, via Sommarive 9, 38123, Trento, Italy

[b] University of Palermo, Department of Engineering, viale delle Scienze, 90128, Palermo, Italy

francesco.galvagnini@unitn.it

Abstract

Nowadays the energy consumption in the construction sector in the European Union covers the 41% of the total energy demand, and it is responsible for the 38% of the greenhouse gases emissions [1]. The buildings energy consumption can be divided into 50-60% for heating, 10-25% for domestic hot water production, 3-10% for cooling and lighting systems [1]. Energy demand in building sector is expected to increase of about 50% in 2050 [2]. For these reasons, it is essential to increase the efficiency of the buildings by applying new materials and technologies to the construction sector [1-3]. Thermal energy storage materials (TES) like phase change materials (PCM) can be combined with insulating materials to produce a new insulating material capable to store thermal energy during the day and releasing it during the night [4]. This material allows to reduce the temperature peak load and to shift it to a better indoor temperature management. In this work polyurethane (PU) insulating panels were produced and combined with different amounts of an encapsulated paraffin, used as Phase Change Material (PCM), to produce multifunctional materials able to store/release thermal energy near room temperature (i.e. around 20 °C). The resulting materials were characterized from a microstructural, thermal and mechanical point of view. Optical microscopy micrographs and density measurements evidenced that the introduction of PCM tends to destroy the cellular structure of PU Foams, and for PCM contents above 30 wt% the foams were characterized by an open cell morphology. Scanning electron microscope (SEM) observations revealed a tendency of the PCM to be distributed in the cell walls intersections, and a limited interfacial adhesion between PCM and PU. Thermogravimetric analysis (TGA) evidenced that the introduction of the PCM tended to increase the degradation resistance of the foams, while from Differential Scanning Calorimetry (DSC) tests it was possible to conclude that PCM addition was able to impart good thermal energy storage properties to the foams, with specific melting enthalpy values of 70 J/g for a PCM content of 50 wt%. As expected, thermal conductivity (λ) of the foams increased with PCM amount, but this enhancement was not directly related to the higher λ of the PCM itself, but rather than to the cell opening effect promoted by the PCM introduction. PCM addition progressively increased the stiffness of the foams, reducing the failure properties both under quasi-static and impact conditions. Moreover, the mechanical properties were strongly affected by the testing temperature (i.e. the physical state of the PCM). It was therefore demonstrated the technical feasibility of producing PU foams containing considerable amounts of PCM, that could be widely used in construction field for a better indoor temperature management.

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P8

Novel 3D printed design to conceive advanced flame retardant polymeric multi materials

Laura Geoffroy, Fabienne Samyn, Maude Jimenez, Serge Bourbigot
Université de Lille, CNRS, ENSCL, UMR 8207, Unité Matériaux et Transformation (UMET), F-59000 Lille, France
laura.geoffroy@univ-lille.fr

Abstract

Nowadays, many fields such as transportation are doing extensive research to elaborate low flammability materials. To make flame retardant (FR) polymeric materials, different ways can be considered. The standard approach consists in modifying the formulation by incorporating FR fillers in the bulk, but the development of novel chemistries becomes harder and is costly. In this work, a novel approach is proposed. Instead of changing the material formulation, the design and the layout of materials are evaluated to reach optimized fire protection performances. Standard polymer shaping processes do not easily allow designing sophisticated shapes without using a complex mold [1], on the contrary to 3D printing, which is a very flexible technique. Among all 3D printing techniques, Fused Deposition Modelling has the best quality to cost ratio, but the range of filaments commercially available is limited and costly. However, in some specific 3D printing processes, no filaments are necessary. Polymers pellets feed directly the printing nozzle, allowing investigating many polymeric matrices with no commercial limitation (Figure 1) [1]. In this work, innovative flame retarded sandwich structures using 3D printing were created with two skins completely filled and a partially filled grid patterned core (Figure 2). In the first part, different grid patterned cores were prepared by varying the infill density (either 30 or 50 %) as well as the fire retardant used in the ethylene vinyl acetate (EVA), containing aluminum tri-hydroxide (ATH) at 30 wt.-% loading [2]. In a second step, biphasic materials containing air, water, potassium carbonate solubilized or in powder form and sodium carbonate inside the porosity of the sandwich core were evaluated in the material (composed on EVA and 30 wt.-% of ATH). A full characterization of the fire properties of these innovative 3D designs were performed [2]. This work is a proof of concept of the usefulness of fused polymer deposition technology to design new flame retarded materials, offering a way to make safer materials at low cost.

Figure 1. Illustration of the additive manufacturing technique used

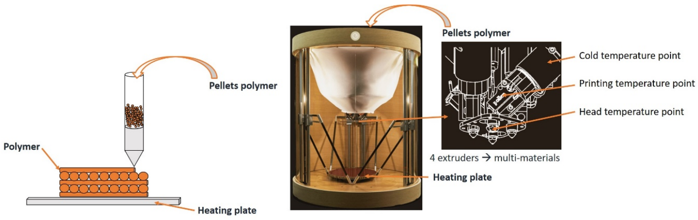
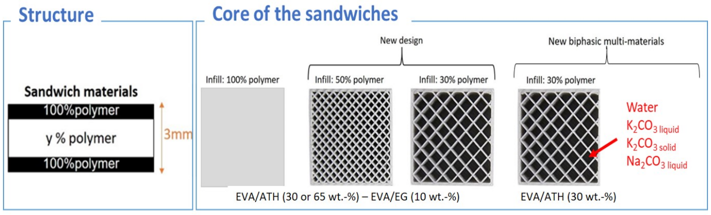


Figure 2. Concepts of flame retardant designs printed using additive manufacturing



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P9

A new biocomposite obtained using poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) and microfibrillated cellulose

Alberto Giubilini,[a] Corrado Sciancalepore,[a,b] Massimo Messori,[b,c] Federica Bondioli[b,d]

[a] Dipartimento di Ingegneria e Architettura, Università di Parma, Parco Area delle Scienze 181/A, 43124, Parma, Italy

[b] INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, via G. Giusti 9, 50121, Firenze, Italy

[c] Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena e Reggio Emilia, via P. Vivarelli 10, 41125, Modena, Italy

[d] Dipartimento di scienza applicata e tecnologia, Politecnico di Torino, corso Duca degli Abruzzi 24, 10129, Torino, Italy

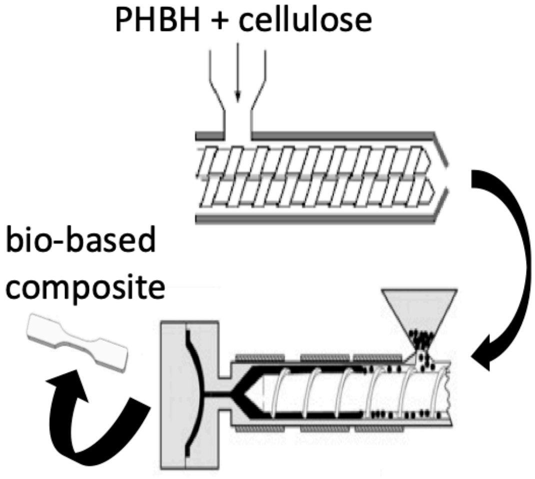
alberto.giubilini@studenti.unipr.it

Abstract

Nowadays, environmental issues are growing in importance due to waste management and depletion of fossil resources. However, modern society is largely based on polymeric materials; and although, it is not reasonable to think to completely remove the use of plastics, it is necessary to start thinking about a more sustainable economy [1]. A key action in this regard is the development of new materials from renewable resources with a sustainable end-of-life. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is a bio-based and biodegradable polyester synthesized by bacteria, belonging to the class of PHAs (polyhydroxyalkanoates). Many studies compounding these biopolymers with a reinforcing agent, such as glass fibers or different kinds of cellulose derivatives have been conducted [2-6]. In this work, microfibrillated cellulose (MFC) was used as filler and it was melt compounded with the matrix. The microfibrillated cellulose was obtained with a pure mechanical treatment of high-pressure homogenization, starting from oat hull fiber, a by-product of the agri-food sector. The effects of filler content and of the silanization procedure onto cellulose fibers were evaluated on thermal, morphological and mechanical properties of composites. SEM and FT-IR analysis showed a good dispersion of the filler in the polymeric matrix, denoting the effectiveness of the surface silanization process. The thermal stability of PHBH composites remains substantially unchanged, and the glass transition temperature marginally increases with the increase of the filler content.

Furthermore, silanized MFC shows slightly reinforcing mechanical effects on PHBH composites, such as the increase of 10% of the Young modulus with an increase of the maximum tensile stress as well. This finding has also an economical interest, since the results showed that MFC, deriving from a by-product, can be successfully used as filler, decreasing the cost of the bio-based compound leaving substantially unaltered its mechanical and thermal properties.

Melt compounding of the PHBH/MFC composites



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P10

Rheological characterization of poloxamine 908 aqueous solutions

Elena Giuliano,[a] Donatella Paolino,[b] Massimo Fresta,[a] Donato Cosco[a]

[a] Department of Health Sciences, University "Magna Græcia" of Catanzaro, Campus Universitario "S. Venuta", viale S. Venuta, 88100, Catanzaro, Italy

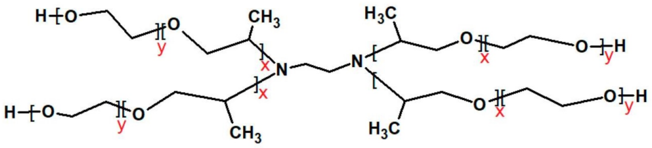
[b] Department of Experimental and Clinical Medicine, University "Magna Græcia" of Catanzaro, Campus Universitario "S. Venuta", viale S. Venuta, 88100, Catanzaro, Italy

elena.giuliano@unicz.it

Abstract

Stimuli-sensitive polymers modulate their structure and physical properties in response to external signals. They are powerful materials to obtain *in situ* forming drug delivery systems. These formulations are viscous liquids before the administration and become gels at body temperature. They are characterized by an easy preparation procedure due to their liquid-like behavior at room temperature, a prolonged residence time at the administration site and a sustained drug release [1]. Amphiphilic copolymers are particularly appealing materials due to their ability of merging the peculiar characteristics of hydrophilic and hydrophobic polymers. Polyoxyethylene (POE) and polyoxypropylene (POP)-based copolymers are widely used in pharmaceutical formulations and are normally classified in two families according to the structure of their main chain. They can be linear tri-blocks called poloxamers or characterized by a X-shaped structure known as poloxamine. Poloxamines are made up of an ethylenediamine central portion linked to four chains of POP- POE [2]. Poloxamines are mainly used in petroleum as anti-foaming and emulsifier agents, and for the development of washing solutions for contact lens thanks to their ability to remove adsorbed proteins and to enhance the comfort feeling. They are also employed as constituents of transdermal formulations, as scaffolds in the tissue engineering and in the development of stealth nanoparticles. Poloxamines can form micellar and gel structures as a function of both temperature and pH. Poloxamine 908 (hereafter, P908) is a highly hydrophilic polymer (21 POP and 114 POE units per arms; HLB>24) widely used as biomaterial [3]. The aim of this investigation was to evaluate the ability of P908 aqueous solutions to form gels and the influence of copolymer concentration and temperature on their rheological properties. Viscosity measurements and the sol–gel transition temperature were investigated by rheological studies. An increase of the polymer concentration increased the viscosity of obtained gels, while the sol–gel transition temperature was decreased. P908 formed thermally reversible gels at a polymer concentration greater than 25% w/w, showing a useful shear thinning behavior at 37 °C. The shear thinning behavior is preferred in the design of an *in situ* gel system because the formulation can be easily injected using low pressure thanks to a temporary destructuration of the polymeric network. Above the sol-gel transition temperature, the systems reverted to Newtonian fluids with a constant viscosity in the range of examined shear rates. Additional investigations are required to evaluate the real effectiveness of the described formulations, the dose and time-dependent toxicity, their *in situ* residence time and the release profiles of entrapped model compounds.

Chemical structure of poloxamines



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P11

Moving beyond perfluorinated polymers: sulfonated poly(biphenyl alkylene)s as ion exchange membranes for alkaline redox flow batteries

Sergio Granados-Focil,[a] Diana De Porcellinis,[b] Michael J. Aziz[b]

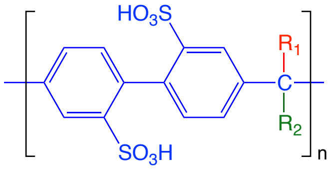
[a] Gustaf Carlson School of Chemistry and Biochemistry, Clark University, Worcester, MA., U.S.A.
[b] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA., U.S.A.

sgranadosfocil@clarku.edu

Abstract

A series of sulfonated poly(biphenyl alkylene)s, SPBAs have been synthesized and tested as candidates for alkaline redox flow battery cation exchange membranes. Free standing films can be cast from solution and used for electrochemical impedance spectroscopy (EIS), GPC, NMR, FTIR and reagent permeability measurements and redox flow battery testing. Ionic conductivity was measured as a function of polymer composition and was found to correlate with the water uptake of these materials. The ionic conductivity of these membranes as measured by EIS was higher or comparable to those measured for Nafion 212. Notably, the permeability of redox-active reagents across these films was at least one order of magnitude lower than the values measured for perfluorinated analogs. NMR and FTIR studies indicate that the polymers remain stable after exposure to strongly alkaline aqueous environments, pH>12, for longer periods of time that those measured for sulfonated PEEK-based materials [1]. During cell resting, these SPBA membranes exhibited power densities higher than those measured for perfluorinated membranes under the same conditions. Thermally crosslinkable or hydrophobic aromatic moieties were introduced into the SPBA backbone to study the effect of polymer chain packing on molecule cross-over, ion transport and water uptake. The effect of polymer composition on the membrane properties and electrochemical cell performance will be discussed.

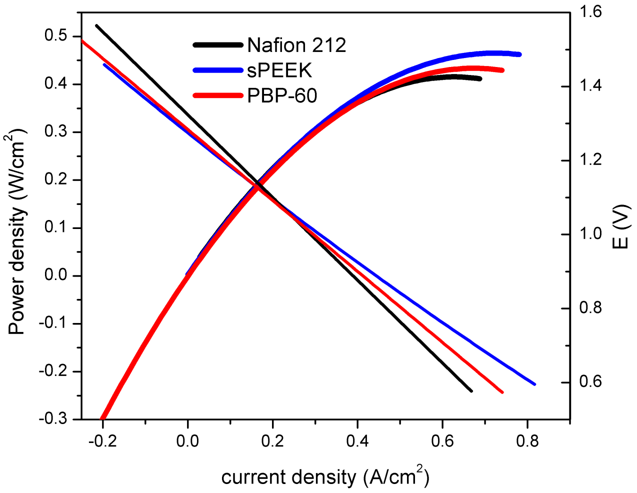
Chemical structure and properties of SPBA



σ= 35 mS/cm (in D.I. water)
IEC= 2.5 mEq/g
Ferricyanide permeability < 1 X 10^{-10} cm^2/s

R$_1$: Hydrophobicity control

R$_2$: Swelling control



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Acknowledgments

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P12

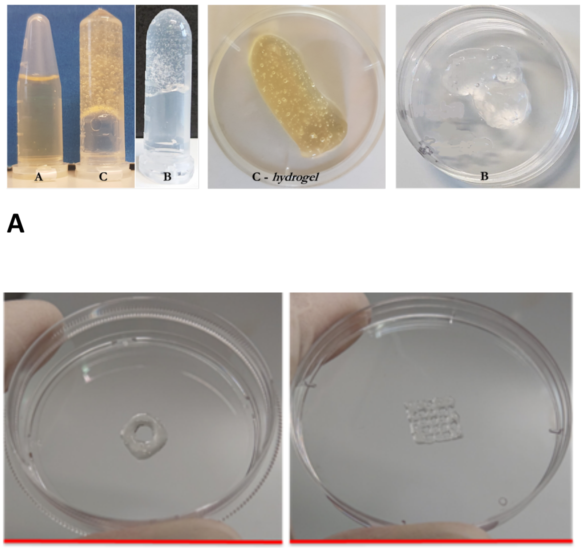
Design, synthesis and biological evaluation of printable hybrid hydrogel formulations for 3D in vitro cell culture applications

Alessia Grittini,[a] Cataldo Pignatelli,[a] Cesare Cosentino,[b] Sabrina Bertini,[b] Francesco Nicotra,[a] Laura Russo[a]
[a] University of Milano-Bicocca, Department of Biotechnology and Biosciences, piazza della Scienza 2, 20126, Milano, Italy
[b] Istituto di Ricerche Chimiche e Biochimiche G. Ronzoni, via G. Colombo 81, 20133, Milano, Italy
a.grittini2@campus.unimib.it

Abstract

In recent years, artificial extracellular matrices (ECMs) have been widely employed as scaffolds in tissue engineering. Also, they can be exploited as scaffold or matrices for 3D in vitro systems or drug screening purposes [1]. With this aim, new biomaterials can be developed to mimic cell microenvironment in both physiological or pathological conditions [1,2]. Artificial ECMs should mimic the hybrid and dynamic characteristics of the natural ECM but also should be constituted by tunable materials, such as to tailor their biological functions as well as physic-chemical and mechanical properties [2]. In addition, the 3D architecture and specific geometries of the scaffold are necessary to control cell differentiation and tissue functionalities [2]. In this work, to mimic lung microenvironment, elastin and hyaluronic acid have been selected as component of the artificial niche. Elastin [3] and hyaluronic acid [4] were opportunely modified with maleimide linkers taking advantage of amino groups on elastin and carboxylic group on hyaluronic acid. Both the polymers have been characterized and used to formulate a hydrogel through PEG dithiol cross linker. The resulting hydrogel was stable, homogenous, with relevant mechanical properties and suitable for 3D printing (Figure 1 and Figure 2). Preliminary in vitro assays were performed to evaluate the biocompatibility of the final material. These data suggested that the hydrogel have the basic properties that allow to proceed the investigation aimed at its usage as bio printed scaffold or 3D models.

Images of hybrid hydrogel



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Ministero della Salute, RICERCA FINALIZZATA 2016 RF-2016-0236294 (1/3/2018-28/2/2021) Theory enhancing Projects. Title: Dissecting the link between pulmonary stromal changes and lung cancer progression for biomarkers discovery and therapeutic intervention.

P13

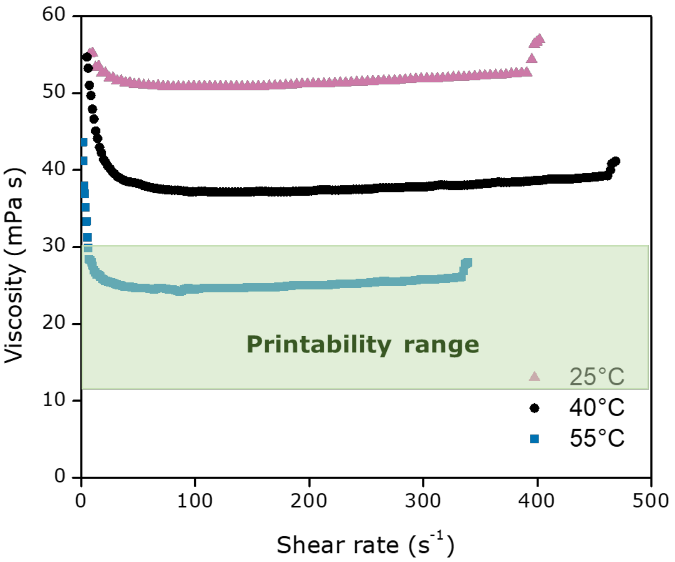
Exploiting additive manufacturing of benzocyclobutene tailoring BCB-based Inks for Ink-jet printing

Filippo Iervolino,[a] Martina Scolari,[b] Laura Castoldi,[b] Marinella Levi[a]
[a] Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133, Milano, Italy
[b] STMicroelectronics, Via Camillo Olivetti, 2, 20864, Agrate Brianza (MB), Italy
filippo.iervolino@mail.polimi.it

Abstract

Benzocyclobutene (BCB) is a thermoset polymer that is widely adopted in the electronic industry. BCB is mainly used as an interlayer dielectric (ILD) due to its low dielectric constant, good planarization, absence of outgassing and limited copper migration [1,2]. Moreover, BCB has the advantage of having a high thermal stability, due to a glass transition temperature (T_g) of ~350°C, compared to other dielectric materials, such as biaxially oriented polypropylene [3,4]. Additive manufacturing (AM), also known as 3D printing, is a recent fabrication technology that generated interest in various fields over the last decade. AM consists in the fabrication of a geometry in a layer-by-layer fashion starting from a Computer-Aided Design (CAD) file [5]. The electronic industry started to investigate this kind of technology due to its versatility and the possibility of fabricating structures in the absence of a mold or a mask. In addition, the use of AM technologies allows printing on non-flat surfaces, simplifies the assembly process, reduces material wastes and product dimensions [6]. Traditional AM technologies, e.g., Liquid Deposition Modeling (LDM), Stereolithography (SLA) and Ink-Jet Printing (IJP), can be used to process thermoset polymers, as well as novel technologies like aerosol-jet printing. Currently, BCB is processed with conventional techniques, such as spin-coating and screen printing, but there is a lack of information in the literature concerning the fabrication with AM technologies. AM would allow the fabrication of complex geometries on different type of substrates, without using any kind of mask [1,6]. Moreover, using AM for the fabrication dielectric materials, such as BCB, opens new possibilities for the electronic industries for different types of application, e.g., ILD, packaging of devices, wafer bonding, MEMS and bumps. Therefore, this work aims to investigate the possibility of processing BCB with AM technologies. More precisely, IJP was used. Printable BCB inks were prepared. The inks were made up of the b-staged BCB polymer and a solvent. The solvents were chosen considering the affinity with the polymer and the ease with which they can evaporate after the printing process. The inks were characterized in order to assess their printability with rheological tests. The ink’s viscosity is the most critical parameter concerning the printability. An ink with a too high viscosity, i.e., > 30 mPas, cannot be printed. Figure 1 shows the results of a rheology test performed on an ink containing BCB and mesitylene (i.e., 1,3,5-trimethylbenzene). Differential Scanning Calorimetry (DSC) was used to assess the thermal properties of the material and evaluate its curing temperature. Thermogravimetric Analysis (TGA) tests were performed to evaluate the thermal stability of the polymer. Then, simple and complex geometries were fabricated with IJP to prove the feasibility of processing BCB with AM technologies.

Figure 1. Rheological tests performed on BCB/mesitylene ink at different temperatures



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P14

Stereoselective copolymerization of linear terpenes with butadiene: a path to more sustainable elastomers

David Hermann Lamparelli,[a] Veronica Paradiso,[a] Francesco Della Monica,[a] Antonio Proto,[a] Silvia Guerra,[b] Luca Giannini,[b] Carmine Capacchione[a]

[a] Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università degli Studi di Salerno, via Giovanni Paolo II 132, 84084, Fisciano (SA), Italy

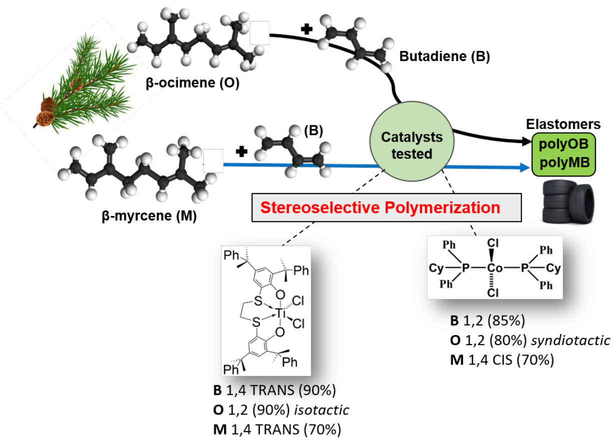
[b] Pirelli Tyre S.p.A. viale Piero e Alberto Pirelli 25, 20126, Milano, Italy

dlamparelli@unisa.it

Abstract

Elastomers are versatile materials capable of filling a wide variety of medical, domestic and industrial products. In particular, the largest consumption of this class of polymers goes in the automotive sector for tire. The production of synthetic rubber that mimic the chemical composition of natural rubber (**NR**), the best-known material of this class, has quickly become one of the main activities in the petrochemical industry to satisfy the growing global demand for rubber [1]. Petroleum, natural gas, coal, oil and acetylene are the raw starting material for the production of synthetic rubber that has greatly surpassed the production of **NR** in the last decades. Recently, huge efforts were made to find alternative ways to produce synthetic elastomers in order to reduce the consumption of non-renewable resources [2]. Terpenes are an important family of hydrocarbons derived from isoprene with cyclic or linear structure and characterized by the presence of conjugated double bonds. They can be considered as alternative bio-based monomers to give access to a large variety of macromolecules, [3-5] including elastomers, or alternatively, can be easy functionalized in order to obtain polyketones, polyesters, polyamides, cycloolefinic polymers via controlled/living cationic polymerization or ring opening polymerization (**ROP**) [6]. β-ocimene (**O**) and its isomer myrcene (**M**), linear monoterpenes readily isolated on an industrial scale from the pyrolysis of pinenes, have already been tested as monomers for the stereoselective polymerization promoted by catalytic systems based on lanthanides [7], iron [8] and titanium [9]. In this study, it has been reported the homopolymerization and the unprecedented copolymerization of **O** and **M** with butadiene (**B**) by soluble titanium and cobalt complexes activated by methylalumoxane. Copolymers compositions were found to be easy tailorable through judicious variations of the alimentation feed. The polymers obtained were completely characterized through gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR).

Copolymerization of terpenes with butadiene



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P15

Quantitative determination of residual isocyanate in polyamide resins

Ezio Leone,[a,b] Serena Gabrielli,[a] Genny Pastore,[a] Lorenzo Spinelli,[b] Giovanni Loggi,[b] Giovanna Biondi,[b] Enrico Marcantoni[a]

[a] Dipartimento di Chimica, Università degli Studi di Camerino, via Sant'Agostino 1, 62032, Camerino (MC), Italy

[b] Elantas Europe S.r.l., Zona Industriale Campolungo 35, 63100, Ascoli Piceno, Italy

ezio.leone@unicam.it

Abstract

Polyamides (PAs) are macromolecules with repeating units linked by amide bonds [1]. PAs have unique thermal, mechanical and electrical properties, which make them versatile products for a broad range of commercial applications. There are several well-established methods to prepare polyamides, including the use of aromatic diisocyanates and carboxylic diacids [2], as reported in Figure 1. However, isocyanates are known for their high toxicity: they are powerful respiratory and cutaneous irritants and sensitizers whose most severe outcome is occupational asthma [3]. In fact, within the European Community (EC), isocyanates used in the manufacture of plastics materials and articles intended to come into contact with operators are regulated by EC Directive 90/128 EC and amendments [4-5]. Residual levels in the finished plastic must not exceed 1.0 mg/kg expressed as –NCO. For this purpose, Elantas Europe, a manufacturer of insulating materials, in collaboration with the University of Camerino, developed a methodology which allows the determination of several –NCO based organic molecules after a very easy and successful derivatization by using HPLC. In particular, 4,4'-diphenylmethane diisocyanate (MDI) and isomers 2,4 and 2,6 of toluene diisocyanate (TDI), were taken into account, in nine different batches of a polyamide resin. A novel HPLC-UV method for isocyanate analysis was settled, allowing the quantification of mentioned monomers in a polyamide matrix. Phenyl isocyanate was derivatized with several amines and used as internal standard, analyses were performed in order to define the best internal standard for this specific application. Pure TDI and MDI were also derivatized and used for the calibration curve. Derivatization of isocyanate groups allows their stabilization and increases their solubility. After the first screening, the resin samples were treated with the derivatizing agent and diluted in organic solvents able to precipitate the polymeric matrix (Figure 2). Preliminary HPLC runs of analytes and samples were carried out in order to find the best chromatographic conditions and avoid any interferences. In the specific case of polyamide resins, at low polymerization degree level, the main issue was related to the complexity of the whole polymeric sample. In fact, while TDI was detected without any problem, as far as MDI was concerned, the analytical peak was cohesive to another one.

This method allowed the determination of several Isocyanate derivatives at very low concentration (<20 ppm).

Figure 1. General synthesis of Polyamide (PA) resins

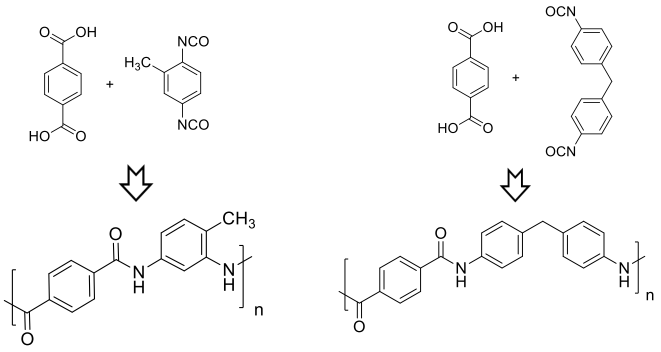
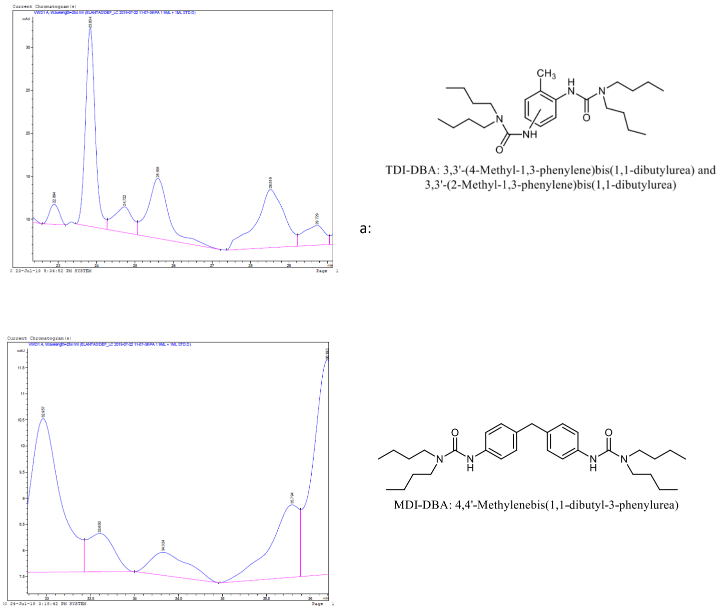


Figure 2. Derivatization of TDI and MDI isocyanates and PAs sample analysis



TDI-DBA: 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dibutylurea) and 3,3'-(2-Methyl-1,3-phenylene)bis(1,1-dibutylurea)

MDI-DBA: 4,4'-Methylenebis(1,1-dibutyl-3-phenylurea)

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P16

Remanufacturing of end-of-life composites from the wind energy sector with styrene-free resins

Marinella Levi, Raffaella Suriano, Andrea Mantelli, Stefano Turri

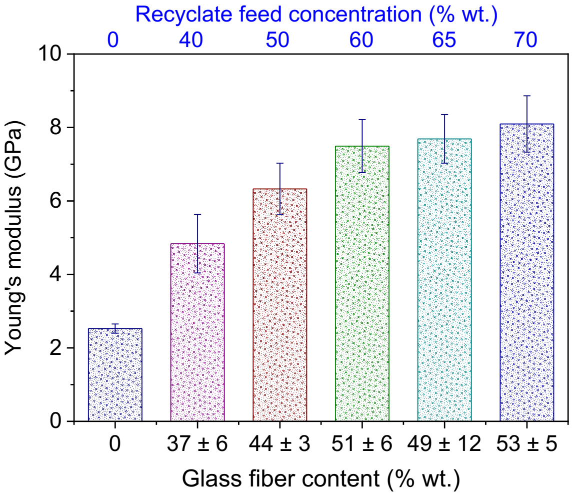
Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, piazza Leonardo da Vinci 32, 20133, Milano, Italy

marinella.levi@polimi.it

Abstract

The demand for new products and their consumption rate are dramatically increasing, due to the exponential grow of human population and the current model of linear economy, which unsustainably consumes natural resources, manufactures and discards products. Consequently, a great number of End-of-Life (EoL) products are continuously being disposed of, leading to a number of environmental problems. Representative examples of EoL products are wind turbine blades, whose annual production volume are expected to increase significantly in the coming decades, reaching 100,000 tons per year in 2034. Wind turbine blades are mainly composed of glass fiber reinforced polymers (GFRPs) and the application of a circular economy approach to EoL GFRPs management is one of the challenges of the modern manufacturing industry [1-2]. Responsible treatments of EoL products that may include reusing, recycling or remanufacturing are desirable and beneficial both environmentally and economically, because waste is minimized, while valuable components and materials are recovered. In the light of the above, this work was focused on the feasibility study of reusing mechanically recycled glass fibers in remanufacturing of composites. Recycled materials were analyzed by thermogravimetric analysis (TGA) to find the actual content of glass fibers, which was 71.5 ± 3%. With the aim of selecting an adequate matrix material for remanufacturing, in terms of processability and mechanical properties, three styrene-free thermosetting binders were studied: an acrylic system; an epoxy resin; and a polyurethane-based resin. Subsequently, the epoxy resin was loaded with different concentrations (40%, 50%, 60%, 65%, 70% wt.) of mechanically recycled glass fibers, in order to find the optimal amount of recyclates usable. These different formulations were tested by means of TGA, differential scanning calorimetry (DSC) and tensile tests to measure the real content of reinforcement phase contained in each sample, their thermal and mechanical properties. By employing the Halpin-Tsai model to predict the elastic modulus of the composites, a good agreement was found between theoretical values and experimental results, obtained by tensile tests. Furthermore, tensile tests were performed on the composites currently employed in commercial applications in order to get a reference value for the desired final properties of the remanufactured items. Some limitations regarding the ultimate tensile properties and the adhesion between the matrix and the fibers as evidenced by scanning electron microscopy (SEM) images were found and must be overcome. Nevertheless, the possibility of using recycled glass fibers as reinforcement phase and of obtaining newly developed composite materials with high values of elastic modulus was demonstrated.

Young's modulus of differently reinforced epoxy-based composites



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P17

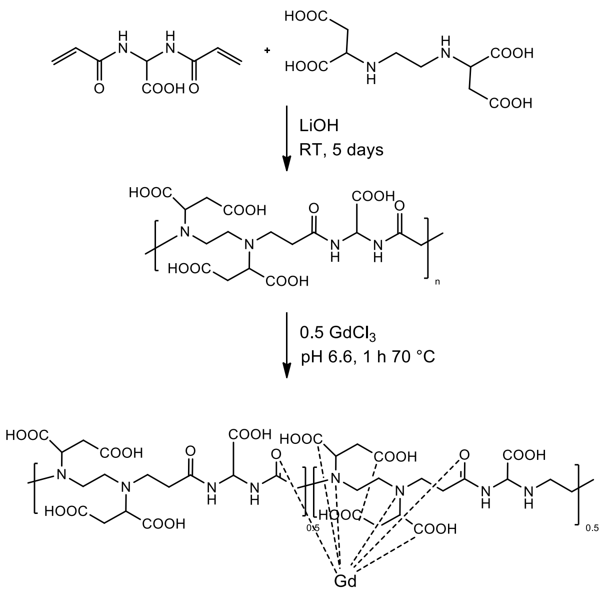
Polydentate ligands and their lanthanide complexes: synthesis and characterization

Daniela Maggioni,[a] Paolo Arosio,[b] Alessandro Lascialfari,[c] Paolo Ferruti,[a] Amedea Manfredi,[a] Elisabetta Ranucci[a]
[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy
[b] Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, 20133, Milano, Italy
[c] Dipartimento di Fisica, Università degli Studi di Pavia, via Bassi 6, 27100, Pavia, Italy
daniela.maggioni@unimi.it

Abstract

Magnetic resonance imaging (MRI) is a diagnostic technique that received a huge development in the last decades. It allows to obtain images of an organism without using invasive methods. Unfortunately, in many cases the natural tissue contrast is not enough to obtain good images. For that reason, many different contrast agents have been developed since the 70s'. Up to date, the contrast agents employed at the clinical level are small molecules, mostly gadolinium chelates, that have as drawback a short blood clearance lifetime that does not allow to influence the tissue biodistribution. On the contrary, binding lanthanide chelates to macromolecule or nanoparticle structures can extend their blood permanence and thus enhance the ability of the macromolecular contrast agent to reach the target. Moreover, the attachment of many lanthanide chelates per macromolecule coil or nanoparticle favorably influence the contrast image since the local concentration increases and the molecular tumbling of the paramagnetic center decreases, and both these two factors contribute to enhance the relaxivity [1]. In this context, a polyamidoamine chelating agent has been prepared and characterized as a new macromolecular nanostructured multi-chelating agent. Polyamidoamines (PAAs) are a family of synthetic polymers obtained by Michael-type polyaddition of primary or secondary amines to bisacrylamides [2]. They are hydro-soluble, biocompatible and biodegradable. Moreover, they show stealth like behavior, and in many cases, they tend to self-assemble giving small nanoaggregates so they have the chance to be passively accumulated at the tumor site by the so called enhanced permeability and retention effect. All these favorable features make PAAs good candidates to behave as effective drug delivery or contrast agent vectors. To prepare the PAA-Gd contrast agent, a suitable PAA, bearing in each repeating unit a ethylendiaminosuccinic acid (EDDS) moiety, has been synthesized (Figure 1, BAC-EDDS) and fully characterized by NMR spectroscopy and size exclusion chromatography (SEC). It was than reacted with $GdCl_3$ affording a white fluffy solid, after purification by the resin "Chelex 100" (to avoid the presence of free Gd(III) ions) and lyophilization. In order to study the thermodynamic formation constant of the chelate on a simplified system, the molecular model compound mimiking the chelating repeating unit has been also successfully synthesized by reacting the acryloilglycine with EDDS in the ratio 2:1, respectively. Its La-chelate complex showed a good stability, comparable to the La-DTPA (DTPA = diethylenetriamine pentaacetic acid). Finally, the relaxivity profiles (r1 and r2) of Gd-BAC-EDDS polymer complex have been measured as well as the phantom MRI images at 8.5 MHz, that showed the great superiority of this polymeric Gd-Chelate with respect to the commercial contrast agent Magnevist.

Synthesis of the BAC-EDDS polymer and its Gd complex



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Acknowledgments

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P18

Polymer-modified liposomes as thermoresponsive nanocarriers for the delivery therapeutic molecules

Maria Isabel Martinez Espinoza, Luisa Mugnaini, Francesco Cellesi

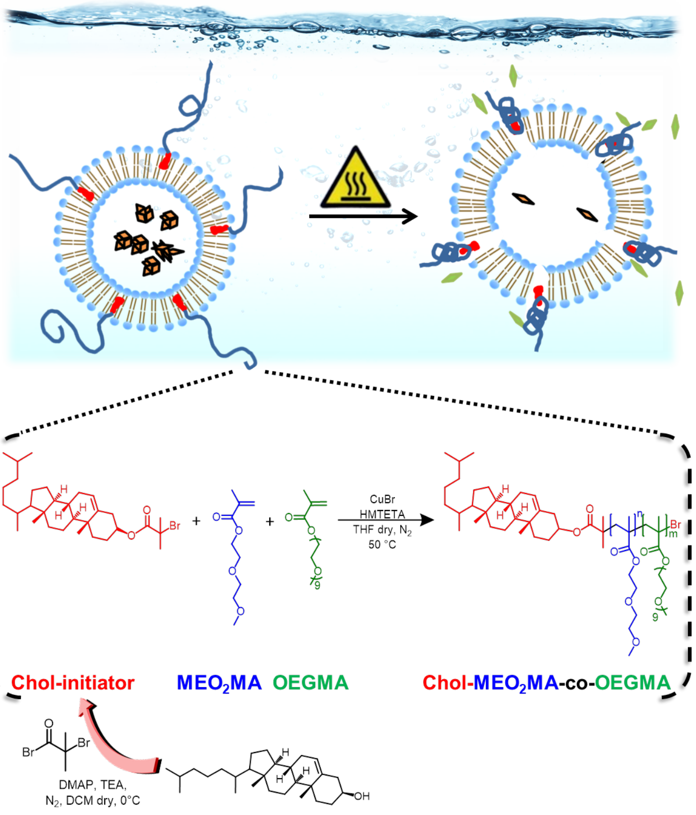
Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta" Polytechnic University of Milan, via L. Mancinelli 7, 20131, Milano, Italy

mariaisabel.martinez@polimi.it

Abstract

Liposomes have invaluable properties such as nano-dimension, the capability of protecting encapsulated payloads from degradation under unfavorable conditions, biodegradability, biocompatibility and non-toxicity. These characteristics have attracted attention in many fields of nanomedicine, where nanocarriers are required for targeted drug delivery. [1] To date, conventional liposomes composed of a lipid membrane and an aqueous nucleus, have evolved into more sophisticated structures through surface functionalization or by incorporating specific lipids or molecules, in order to modulate the final properties of these nanocarriers. [2-3] In particular, thermosensitive liposomes are composed of lipid membranes which present a phase transition slightly above the physiological temperature, and represent a promising tool for targeted drug delivery when used in combination with local hyperthermia. [4-5] Thermo-sensitive polymers, such as the N-Isopropylacrylamide (NIPAM), have recently been used to modulate temperature sensitization, release behavior and surface properties of liposomes. [6] Lutz et al. published the preparation of a PEG-based copolymer that has a lower critical solution temperature (LCST) [7-8], and can also be used for modulating the phase transition of liposomal nanocarriers. [1-2] In this study, a PEG-based copolymer was synthesized via Atom Transfer Radical Polymerization (ATRP) using a cholesterol-functionalized initiator, which allow the polymer chain to anchor to the lipid bilayer of liposomes. The thermoresponsive cholesterol-functionalized PEGylated copolymer (Chol-OEGMA-co-MeO$_2$MA) was used to formulate thermo-responsive vesicles, and to investigate their physicochemical properties, including drug loading and release.

Synthesis of the Chol-OEGMA-co-MeO2MA -functionalized liposomes



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P19

Polyamide 6 and halloysite nanocomposites to improve polymer shelf-life: study on filler physicochemical properties, functionalization and dispersion technique

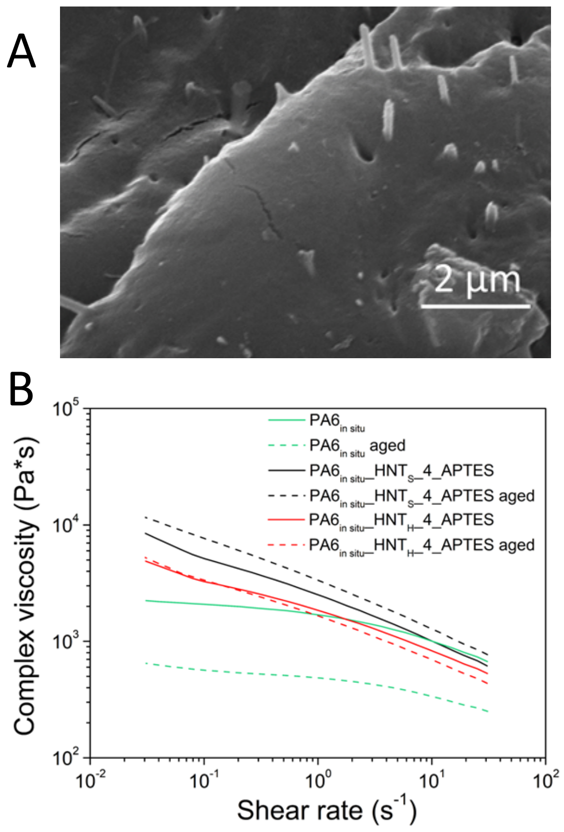
Daniela Meroni,[a,b] Tommaso Taroni,[a,b] Valentina Sabatini,[a,b] Riccardo Rampazzo,[a,b,c] Marco Bompieri,[a] Daniela Maggioni,[a] Marco Aldo Ortenzi,[a,b,c] Silvia Ardizzone[a,b,c]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy
[b] Consorzio INSTM, Via Giusti 9, 50121, Firenze, Italy
[c] CRC Materials & Polymers (LaMPo), Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy
tommaso.taroni@unimi.it

Abstract

Polyamide 6 (PA6) suffers from fast degradation in humid conditions due to hydrolysis of amide bonds, which limits its durability [1]. The addition of nanotubular fillers represents a viable strategy to overcome this issue, although the additive/polymer interface at high filler content can become privileged site for moisture accumulation [2,3]. As a cost-effective and versatile material, halloysite nanotubes (HNT) were adopted to prepare PA6 nanocomposites with very low loadings (1-4% w/w). The roles of the physicochemical properties of two differently sourced HNT, of filler functionalization with (3-aminopropyl)triethoxysilane (APTES) and of dispersion techniques (in situ polymerization vs. melt blending) were investigated. The aspect ratio and surface charge of the two HNT proved crucial in determining their distribution within the polymer matrix. In situ polymerization of functionalized HNT leads to enclosed and well-penetrated filler within the polymer matrix (Figure A). PA6 nanocomposites crystal growth and nucleation type were studied according to Avrami theory, as well as the formation of different crystalline structures (α and γ forms). After 1700 hours of hydrothermal ageing at 90°C, functionalized HNT reduced the diffusion of water into the polymer, lowering water uptake after 600 h up to 90%, increasing the materials durability also regarding molecular weights and rheological behavior (Figure B).

Characterization of PA6_HNT nanocomposites



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P20

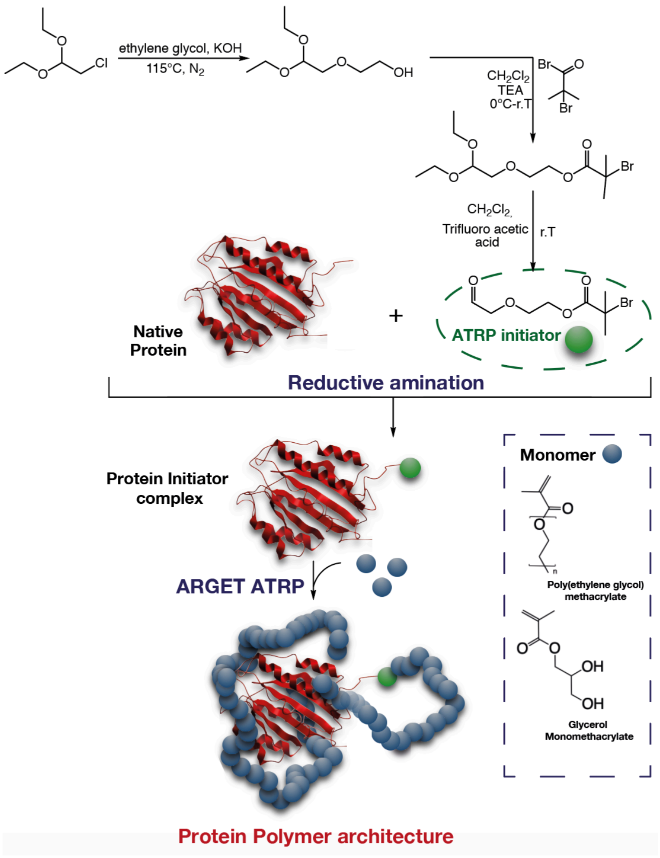
Therapeutic protein-polymer conjugates synthesized through a “grafting from” approach

Filippo Moncalvo, Elisa Lacroce, Francesco Cellesi
Department of Chemistry, Materials and Chemical Engineering “G. Natta’’ Politecnico di Milano, via L. Mancinelli 7, 20131, Milano, Italy
filippo.moncalvo@polimi.it

Abstract

The impact of therapeutic proteins in healthcare is steadily increasing, due to advancements in the field of biotechnology and a considerable understanding of several pathologies. However, the safety and efficacy of their administration is often limited by poor pharmacokinetics, short circulation half-life, denaturation and immunogenicity [1]. The conjugation of biocompatible pre-synthetized polymers to proteins via “grafting to” approach represents a successful strategy for overcoming these limitations [2]. However, in several cases, it may be difficult to obtain high product yield after purification procedures, and narrow molecular weight distributions (low dispersity), although these properties are required for approval by the regulatory authorities [3]. Therefore, a site-specific protein modification, combined with controlled living polymerization techniques and “grafting from” approach, is preferred for this purpose [4,5]. In this project, a “grafting from” approach based on Activator ReGenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP) in aqueous media, was investigated to design novel therapeutic protein-polymer conjugates. Firstly, a functional aldehyde-ATRP initiator was synthesized via a reaction with 2-chloro-1,1-dimethoxyethane and ethylene glycol under basic conditions, followed by acylation with 2-bromoisobutyryl bromide. Afterwards, aldehyde deprotection was achieved under acidic condition. A reductive amination was carried out at different pH (from 5.8 to 6.5) in order to obtain a selective modification on N-terminal of the protein. The reductive amination was selected to guarantee product uniformity, and maximize the activity of the protein, with the binding domain far from the N-terminal group. Lysozyme was used as a protein model at this stage. This protein-initiator conjugate was used for the controlled-living polymerization of poly(ethylene glycol) methacrylate (PEGMA) or glycerol mono-methacrylate (GMMA) via ARGET ATRP in physiological buffers. The reductive amination was sufficiently selective for N-terminal at pH 5.8 - 6.1. ARGET ATRP (carried out in PBS 100 mM) allowed a better level of control of the reaction, compared to PBS 10 mM for different degree of polymerizations (DP). First-order polymerization kinetics were detected in both cases. Under optimized conditions, the dispersity (Mw/Mn) were < 1.4, which indicated a relatively narrow distribution of the molecular weights. Due to the versatility of this strategy in terms of polymer composition, targeted molecular weight and final macromolecular architecture, different therapeutics proteins as neurotrophins and antibodies may be conjugated and tested for different applications

Synthesis of Protein Polymer conjugates through ARGET ATRP and “grafting from” approach



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P21

Development and Characterization of Scaffolds based on Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and Poly(D,L-lactide-*co*-glycolide) (PLGA) for Bone Tissue Regeneration

Gianni Pecorini, Dario Puppi, Simona Braccini, Federica Chiellini

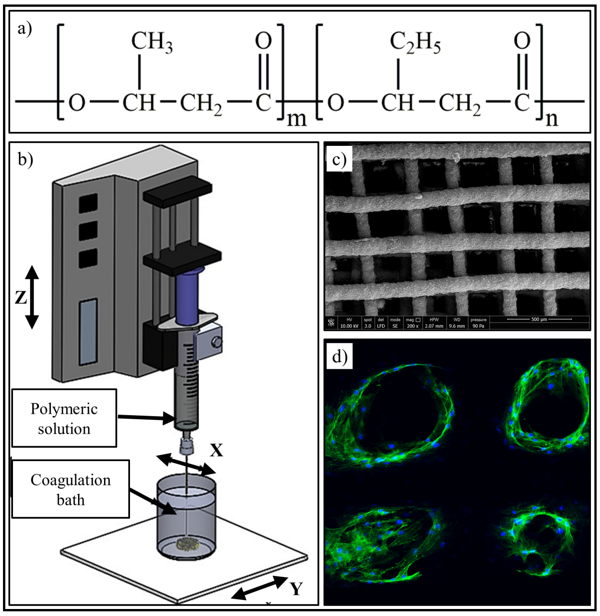
BIOlab Research Group, Department of Chemistry and Industrial Chemistry, University of Pisa, UdR INSTM-Pisa, via G. Moruzzi 13, 56124, Pisa, Italy

gianni.pecorini21@gmail.com

Abstract

Polyhydroxyalkanoates (PHAs) are polyesters synthetized by different kinds of microorganisms and accumulated in granules in the cytoplasm [1]. Their synthesis by means of sustainable processes, with potential for large-scale industrial production, together with their biocompatibility, biodegradability in physiological environment good processing versatility and their superior mechanical properties, in comparison with other polymers from natural resources, make PHAs unique polymer candidates for advanced research in biomedical fields like Tissue Engineering (TE) [2]. TE is a therapeutic field directed towards long-term repair and replacement of failing biological tissues and organs, bringing together the scientific disciplines of materials science, biology and biomedical engineering [3]. It involves the use of three-dimensional, porous, biodegradable structures, generally named as “scaffolds”, promoting cells adhesion and proliferation, the formation of extracellular matrix and acting as a support to the newly formed tissue. Depending on chosen materials and TE strategy, different processing techniques and methodologies, like Additive Manufacturing (AM) techniques, have been proposed to optimize scaffolds external shapes, sizes, surface morphologies and internal architectures. AM is defined as “the process of joining materials to make object from three-dimensional model data, usually layer upon layer” (ASTM 2012). It enables 3D structures with predefined geometry and size to be obtained, and those structures can be also characterized by a porous architecture with a fully interconnected network of pores with customizable size, shape and distribution [4]. In this contribution scaffolds from polymeric blends consisting of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), a biopolymer belonging to the family of PHAs (Figure a), and of poly(D,L-lactide-*co*-glycolide) (PLGA), a polyester approved by Food and Drug Administration (FDA) have been manufactured for biomedical use. The fabrication of these scaffolds has been carried out using Computer-Aided Wet-Spinning (CAWS), an AM technique based on the extrusion of a polymeric solution directly into a coagulation bath and the computer-controlled deposition of the resulting polymeric fiber (Figure b). The presence of porous architectures with fully interconnected networks of pores has been demonstrated for all the developed PHBV/PLGA scaffolds (100:0, 90:10, 80:20, 70:30, 60:40, 50:50 weight ratio between the two polymers) by Scanning Electron Microscopy (SEM) analysis (Figure c) and the pore size turned out to be of the order of hundreds of microns. Wettability of the scaffolds has been evaluated through contact angle measurements, highlighting differences correlated to blend composition, pore size and surface morphology. Thermal and mechanical characterization revealed that scaffold properties could be tuned in a certain range by varying the ratio between the two blend components. A biological evaluation performed by employing the murine pre-osteoblast cell line MC3T3-E1, indicated the suitability of the scaffolds to support a good cell colonization and their capability to promote cell differentiation towards an osteoblastic phenotype. These data have been also confirmed by visualization of cell morphology and scaffold colonization performed by confocal laser scanning microscopy (Figure d).

Development and characterization of PHBV/PLGA scaffolds: a) chemical structure of PHBV; b) schematic representation of Computer-Aided Wet-Spinning (CAWS) apparatus; c) representative SEM image of PHBV/PLGA scaffolds; d) representative confocal laser scanning microscopy image showing MC3T3-E1 cells cultured on PHBV/PLGA scaffolds



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P22

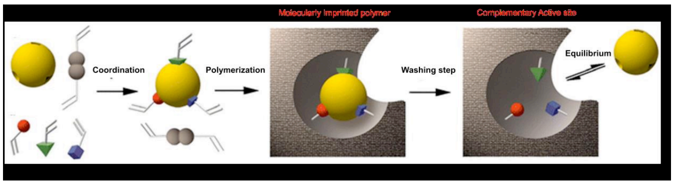
A molecularly imprinted polymer as biomimetic receptor in sensing devices for furfural

Maria Pesavento,[a] Raffaela Biesuz,[a] Antonella Profumo,[a] Daniele Merli,[b] Nunzio Cennamo,[b] Luigi Zeni[b]
[a] Dipartimento di Chimica, Università degli Studi di Pavia, via T. Taramelli 12, 27100, Pavia, Italy
[b] Dipartimento di Ingegneria, Università della Campania Luigi Vanvitelli, via Roma 29, 81031, Aversa (CE), Italy
maria.pesavento@unipv.it

Abstract

A molecular imprinted polymer (MIP) is a synthetic solid containing special sites at which a molecular substrate can combine with high specificity [1]. As seen in the figure, in principle, the synthesis is based on the formation in a liquid phase of an aggregate between some functional monomers and the target molecule, and the subsequent polymerization of the aggregate in the presence of a cross linking agent. The target is extracted from the solid by suitable eluting procedures, leaving pocket sites with a shape complementary to that of the target as dimension and position of the functional moieties. The analogy of these pockets with the interaction sites in the bioreceptors as for example antibodies is evident. MIPs can be obtained in different forms, from large bulky mass to thin layers to nanoparticles, and can be connected to a transductor in different ways. In this case, a sensor is obtained, i.e. an analytical device by which a target can be detected and quantified by a rapid, easy and low cost procedure, particularly suitable for in-situ determinations. Here a MIP especially synthesized for furfural (2-furaldehyde, 2-FAL), a small molecule with an interest in food, biofuels and environmental controls, is presented. The MIP was obtained by thermal polymerization of a mixture of 2-FAL (target), methacrylic acid (active monomer), and divinyl benzene (cross-linker) at molar ratio 1:4:40, and azobisisobutirronitrile (polymerization catalyst). It was used as a biomimetic receptor for chemosensors with electrochemical, on screen printed cell (SPC), and surface plasmon resonance (SPR), on optical fiber, transduction. In both cases MIP was synthesized directly over the transduction surface by in situ polymerization, as a thin layer. A small volume (5-30 µL) of prepolymeric mixture was dropped over the surface and spread by spinning. The polymerization was carried out open air at 72°C for 14 h. The layers obtained were reproducible, and with a good adhesion to the substrates, namely a gold thin layer in the case of SPR transduction, and graphite ink for electrochemical transduction. The sensors were characterized by determining the binding curves. The presence of two different kinds of sites was evidenced by the two transduction methods, according to their different sensitivity. The most sensitive transduction, SPR on optical fiber, detected sites with affinity constant (Kaff) as high as 3.6×10^5 M^{-1}, while the less sensitive electrochemical transduction on SPC, detected sites with Kaff as low as 4×10^2 M^{-1}. The formation of sites with different affinity for the target in MIPs is well known [2]. Thus the same MIP can be used for sensing purposes at different concentration levels using different transduction methods.

Synthesis of molecular imprinted polymer (MIP)



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P23

Characterization of macro and microplastics using near infrared technology and chemometrics

Monika Rani,[a,b] Claudio Marchesi,[a,b] Stefania Federici,[a,b] Laura E. Depero[a,b]

[a] Department of Mechanical and Industrial Engineering, University of Brescia, via Branze 38, 25123, Brescia, Italy

[b] Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali, via G. Giusti 9, 50121, Firenze, Italy

m.rani@unibs.it, c.marchesi003@unibs.it

Abstract

Plastics are probably one of the most important materials for our current way of living, but unfortunately once discarded, they end up in landfills and oceans where they persist for more than 100 years. Microplastic are plastic pieces less than 5 mm along their longest dimension [1], either produced intentionally or fragmented by the natural forces (water current, light, and wind action). It becomes more important to study and devise methods by which they can efficiently identify the plastic pieces according to the polymer class that they belong to. A fundamental issue in their assessment is the lack of standardized protocols for their detection, sampling and fast identification methods. The use of Miniaturized Near-Infrared (MicroNIR) Spectrometer coupled with chemometric tools has shown a great potential in the analysis and classification of the most common polymers. In this work, we used a miniaturized handheld MicroNIR to study plastic waste collected from a recycling plant and microplastic mixture fragmented in the lab. Based on the Resin Identification Code, 250 plastic samples were used for macroplastic analysis and to set up a library of polymers. Subsequently, MicroNIR spectra were analyzed through the application of multivariate modelling. Principal Components Analysis (PCA) was used as unsupervised tool to find trends within the data (Figure 1). In the new sub space determined by the first two PC components, polymers formed very tight and homogeneous clusters. After the exploratory PCA analysis, a supervised classification tool was applied in order to distinguish the different plastic classes. For the microplastic analysis, the three most abundant polymers in the plastic litter: PE, PP, PS were mechanically fragmented in the laboratory to micron size. The distinctive arrangement of blends of these three microplastics were prepared in line with the ternary composition plot (Figure 2). After the PCA exploratory analysis, a quantitative model Partial Least Squares Regression (PLSR) allowed to predict the percentage of microplastics in the mixtures. PLS was calibrated with 42 data-points (Figure 2, blue markers). The model was used to predict the composition of 21 unknown mixtures of the test set (Figure 2, red markers). The advantage of the consolidated NIR Chemometric approach lies in the quick evaluation of whether the sample is contaminated, coloured or not and with no sample pre-treatment [2]. The technique can be utilized with bigger example volumes and even considers an on-site evaluation and in this manner satisfies the need for a high-throughput strategy.

Figure 1: Principal components analysis carried out on urban plastic waste samples

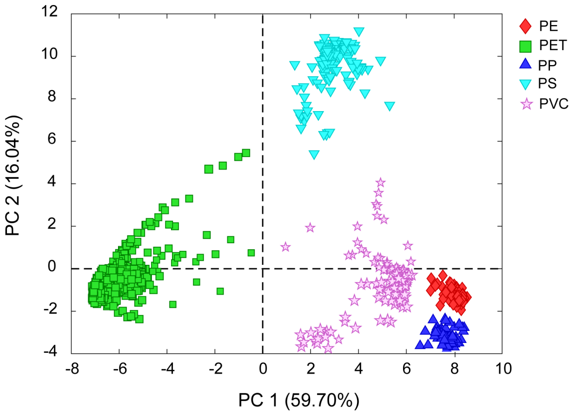
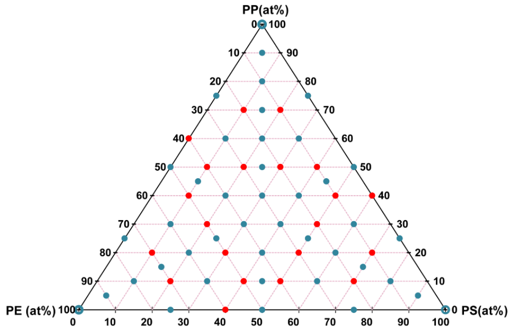


Figure 2: Tri-axial experimental design of PE-PP-PS microplastics. (Blue markers: training data-points; red markers: test data-points)



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P24

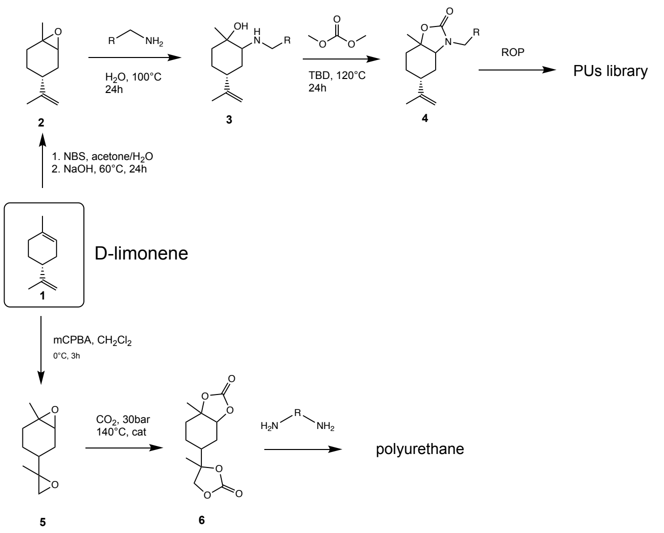
Isocyanate-free polyurethanes from terpenes: ROP of five-membered cyclic carbamates and cyclic carbonates

Lucia Rubino, Vincenzina Barbera, Roberto Guadagnin, Maurizio Galimberti
Deparment of Chemistry, Materials and Chemical Engineering “G. Natta”, Politecnico di Milano, via Mancinelli 7, 20131, Milano, Italy
luciarita.rubino@polimi.it

Abstract

Polyurethanes (PUs) are among the most important polymers, with an annual production of about 5 mass % of total worldwide polymer production. They are very versatile polymers, as they can be thermoplastic, elastomeric, thermoset and foams. PUs are formed by the reaction between polyols and isocyanates. Isocyanates are known to present concerns from the point of view of their impact on environment, health and safety. They are produced from the reaction of amines with toxic phosgene and have several potential negative effects on the human health. In our Group we have been working on innovative polyurethanes with particular attention for sustainable synthesis of PUs [1]. The present work is based on the synthesis of isocyanate-free polyurethanes from terpenes (D-limonene) as bio building blocks, adopting different strategies, such as:

(i) Ring Opening Polymerization (ROP) of cyclic carbamates prepared via dialkyl carbonate (DAC) chemistry [2]. The epoxide ring opening by amines in hot water gives β-amino alcohols, that can react with DACs to yield 5-membered cyclic carbamates. A library of PUs is obtained from the ROP of cyclic carbamates (ii) Ring Opening Polymerization (ROP) of cyclic carbonates by diamines. The (bis)cyclic carbonate of D-limonene can be obtained by reacting limonene diepoxide with CO_2 at 30 bar and 140°C [3].



Synthesis of isocyanate-free polyurethanes from terpenes

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P25

Triple-functional riboflavin macromolecules as a macroinitiator, oxygen scavenger and reducing agent in miniemulsion ARGET ATRP

Karolina Surmacz,[a] Paweł Chmielarz[b]

[a] Doctoral School of Engineering and Technical Sciences at the Rzeszów University of Technology, Al. Powstańców Warszawy 8, 35-959 Rzeszów, Poland

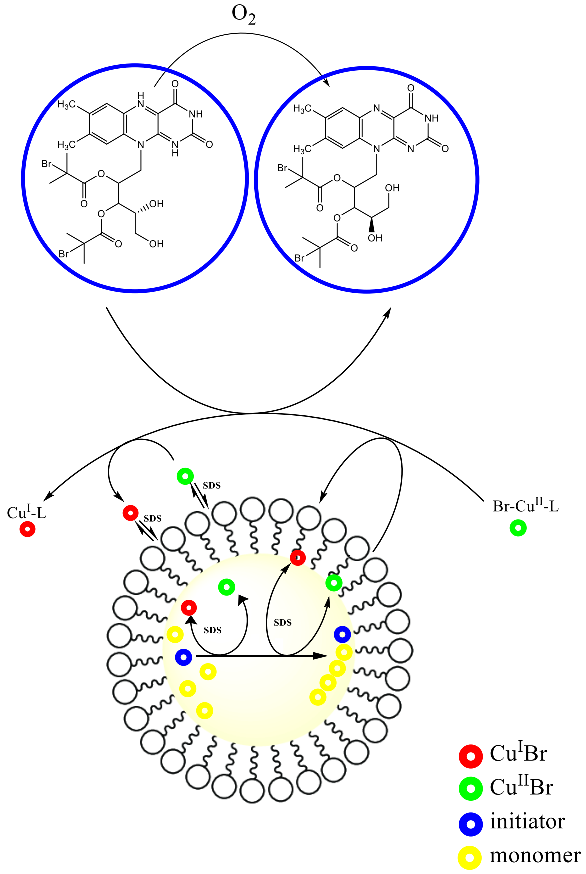
[b] Department of Physical Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

d503@stud.prz.edu.pl

Abstract

Activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) method media was successfully applied in miniemulsion media to obtain precisely defined poly(n-butyl acrylate) (PBA) arms grafted from multifunctional riboflavin core. This is one of the first well-controlled aqueous ATRP process conducted in the open air conditions [1]. The hydrophilic-hydrophobic riboflavin macromolecule was responsible for three crucial mechanisms – interfacial and ion-pair catalysis (single-catalyst approach) [2], continuous reduction of Cu^{II} to Cu^{I} and an efficient oxygen scavenging from the reaction system (Scheme1) [3]. Riboflavin, also known as vitamin B_2, which is involved in the transportation of oxygen to the cells [4], in polymerization reactions can be used as oxygen scavenger. The essential part of this molecule is the isoalloxazine ring responsible for undergoing oxidation-reduction reactions, photosensitivity and catalytic activity [5,6]. The second one part attached to ring moieties is a ribitol tail with four functional hydroxyl groups, which were modified by bromide in order to receive an effective initiator for polymerization processes. Thanks to the preservation of two hydroxyl groups in a ribitol tail of the riboflavin-based initiator, it is possible to places them on the surface of micelles. Pickering emulsion system [7] that enables effective polymerization even with the extremely low weight of a copper catalyst (up to 1 ppm). This macromolecule turns out to be an excellent macroinitiator in the controlled preparation of well-defined homopolymers with narrow molecular weight distribution.

Scheme 1: Reactions of riboflavin-based molecule



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P26

Modulating knots localization in weak ring-shaped polyelectrolytes

Andrea Tagliabue,[a] Lorella Izzo,[b] Massimo Mella[a]

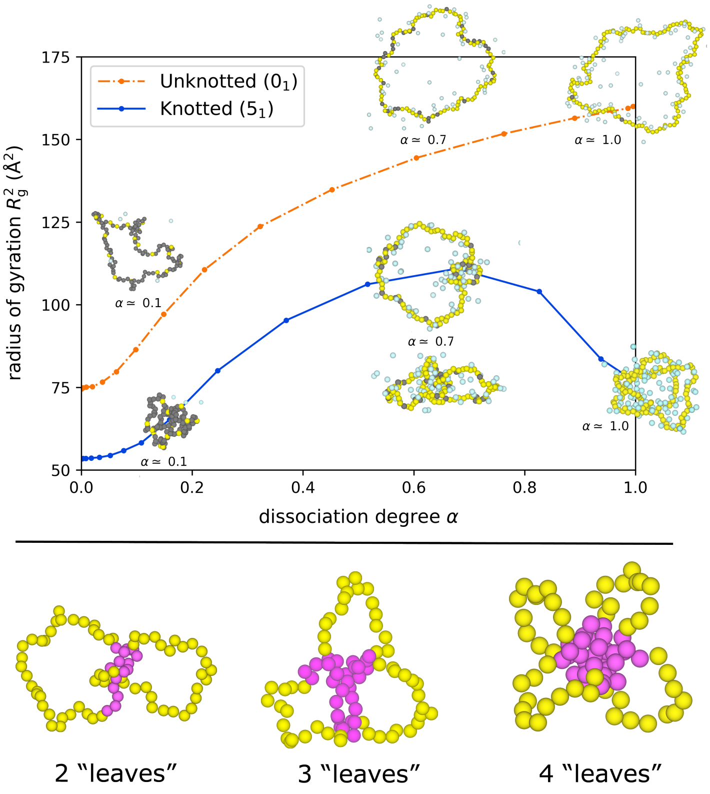
[a] Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100, Como, Italy

[b] Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, via J. H. Dunant 3, 21100, Varese, Italy

a.tagliabue7@uninsubria.it

Abstract

Due to their intrinsic flexibility, polymers are easily deformable and, hence, possibly subjected to topological constraints such as knots; the latter can be temporary, as in linear polymers or entangled chains, or permanent, as in circular or cross-linked species. Understanding the impact on the system properties of such constraints has recently attracted interest due to the fact that knots naturally occur in long DNA chains (either linear or circular)[1] and proteins[2], and as a consequence of the development of techniques that allow to synthetize polymers with very complex topologies. Among polymers, weak polyelectrolytes represent a family of responsive materials whose properties depends on the specific chemical environment, with details such as pH, salt valency and concentration, and chain topology markedly modifying the behavior of the titratable groups. With the aim to understand how knots affect the behavior of weak ring polyacids, we performed theoretical simulations finding that the knot tightness (and, consequently, the polymer size) can be modulated by modifying the pH, the ionic strength of the solution, and/or the solvent quality in a non-trivial fashion. Our simulations evidence that the gyration radius (R_g^2) of ring-shaped polymer does not monotonically increases with the dissociation degree (α) as in "canonical" polyelectrolytes, the knot tightening as α increases from 0 to ~0.8 (i.e., R_g^2 increases), and loosening again (R_g^2 decreases) as the chain further ionizes (see the top panel of the figure); the turning point shifts to lower α values as the knot complexity increases. Moreover, we found ranges of pH at which both conformational states can be populated. Our results suggest a strong interplay between ionized monomers Coulomb repulsion and the ability of counterions to localize on the chain in defining the conformations of flexible polyacid rings, with evidences of a strong correlation between R_g^2 and the fraction of "condensed" counterions. Playing a role in determining this interplay, there is also the "annealing" nature of monomer charges, the tight knot conformations possibly concentrating neutral beads inside the knot itself to reduce its energy. Furthermore, we investigated the impact of the solvent Bjerrum length and the background salt valency and concentrations, finding that conformations with a loose knot become dominant at the equilibrium as the solvent screening power decreases or the monovalent salt concentration increases. Divalent cations, instead, induce a collapse of the polyelectrolyte as already observed for linear [3] and star-shaped [4] morphologies. Finally, we investigated the possibility to "force" knot localization on a small portion of the chain (at least within specific ranges of pH) by inserting sequences of particular features such as non-titratable or solvophobic monomers, or functional groups able to induce monomer clusterization via, e.g., the formation of charged H-bonds[5]. We also predicted the possibility to synthesize species able to assume specific shapes when close to full ionization by inserting various numbers of such sequences along the chain (see the examples shown in the bottom panel of the figure).



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P27

Evaluation of the role of devulcanized rubber on the thermo-mechanical properties of Ethylene-Propylene Diene Monomers (EPDM) foams

Francesco Valentini, Andrea Dorigato, Alessandro Pegoretti
University of Trento, Department of Industrial Engineering and INSTM Research Unit, via Sommarive 9, 38123, Trento, Italy
francesco.valentini@unitn.it

Abstract

In 2010 the world consumption of rubber has been 24.8 kton and in 2017 natural rubber was included by the European Commission in the list of the Critical Raw Material [1]. In spite of the different available techniques to manage End of Life Tyres (ELT), the most common way is to deposit them into landfills. It is estimated that around 800 million tyres are discarded around the world every year [2]. In the European Union the landfilling of ELT tyres is forbidden since 1999 [3]. Recovered waste tyres, due to their composition, can be source of valuable raw materials. An important recycling process of rubber is the de-vulcanization, i.e. the breaking of the sulphur-carbon or the sulphur-sulphur bonds within the polymer chains, in order to obtain a rubber compound that could be processed and vulcanized similarly to virgin rubber [4]. In this work different amounts of both devulcanized rubber (DR) and non-devulcanized rubber (NDR) were added through melt compounding to an Ethylene-Propylene Diene Monomer (EPDM) rubber. The resulting materials were then foamed by using Azodicarbonamide, and the effect played by DR/NDR addition on the thermo-mechanical properties of the obtained foams was evaluated. FESEM micrographs evidenced that devulcanized rubber particles seemed better encapsulated within the EPDM matrix with respect to the corresponding NDR ones, and the better interfacial adhesion was probably a consequence of the re-vulcanization process in which the free crosslinking sites that typically characterize DR are involved. Thermogravimetric analysis showed that the addition of recycled rubber (both DR and NDR) led to a to a slight worsening of the thermal degradation stability, with a decrease of the onset degradation temperature. The incorporation of recycled rubber (both DR and NDR) within EPDM foams led to interesting results in terms of quasi-static mechanical properties. In particular, with the addition of 20 wt% of DR the elongation at break was significantly improved with respect to the neat EPDM foam. Tensile impact behavior of EPDM/recycled rubber foams highlighted a strong improvement of the normalized total absorbed energy, of the normalized impact strength and of the elongation at break with respect to the neat EPDM foams for all the investigated compositions, and especially with a DR content of 20 wt%. It was therefore demonstrated the technical feasibility of producing EPDM foams containing considerable amounts of devulcanized rubber, that could be used in a wide range of applications, reducing the costs related to the raw materials and improving the environmental sustainability of rubber-based products.

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P28

PE based polyurethane/leather yellowing in footwear industry: a case study

Riccardo Vallesi,[a] Alberto Frattali,[b] Maura Pellei,[a] Massimo Biagioli,[b] Francesco M. Iaccarino,[b] Carlo Santini[a]

[a] School of Science and Technologies, Chemistry Division, University of Camerino, via Sant'Agostino 1, 62032, Camerino (MC), Italy

[b] Delta S.p.a., via Sandro Pertini 88/92, 62012, Civitanova Marche (MC), Italy

riccardo.vallesi@unicam.it

Abstract

PU (PolyUrethane) was firstly invented and introduced in the market in the first half of the 20th century. Recently, its economic value has been grown constantly [1,2]. In a worldwide view, PU represents only 5% of the consumption of polymers [3]. There are two different types of PU: Poly-Ether (PE) PU and Poly-Ester (PES) PU. They differ for their chemical structure, reactivity and mechanical properties. However, for the PE polyurethane, colour is an important parameter to be considered. A low colour value increases the commercial value meaning that polyether structure has been unaltered without chain destruction and formation of new compounds. IR analysis shows that this parameter is connected to carbonylic groups next to double-bonds [3]. A large number of normative of International Standard Organisation (ISO) requires a high value on the grey scale. The yellowing of PE PU, in footwear industry, in particular types of articles, can be linked to yellowing of the synthetic leather. In particular, some degradation products can react with the refinement agents of the leather. This situation has been analyzed by different point of view (chemical and physical analyses) in order to have a better understanding of this drawback and to find a solution of the problem.

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P29

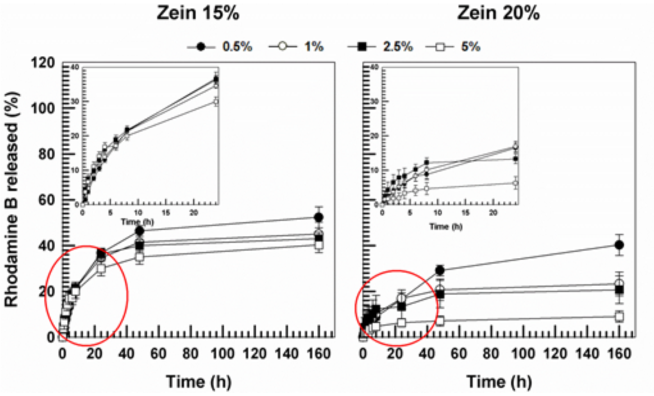
Rheological features of zein-based gels containing model compounds

Silvia Voci,[a] Agnese Gagliardi,[b] Donatella Paolino,[b] Massimo Fresta,[a] Donato Cosco[a]
[a] Department of Health Sciences, University “Magna Græcia” of Catanzaro, Campus Universitario “S. Venuta”, 88100, Catanzaro, Italy
[b] Department of Experimental and Clinical Medicine, University “Magna Græcia” of Catanzaro, Campus Universitario “S. Venuta”, 88100, Catanzaro, Italy
silvia.voci@studenti.unicz.it

Abstract

Many natural polymers are currently used as gelling agents in biomedical and pharmaceutical applications. In this investigation, the influence of various probes on the rheological properties of gels made up of zein, a protein of corn, was evaluated in order to characterize the systems as a function of the polymer concentration. The release profiles of probes from the protein network were evaluated by the dialysis method. Zein dispersions were obtained by the addition of various amounts of biopolymer (10%, 12.5%, 15%, 20% w/v) to a hydroalcoholic solution, under constant, slow magnetic stirring at room temperature to favor the evaporation of the organic solvent and the gel formation. The rheological properties of the formulations were measured by means of diffusive wave spectroscopy (DWS) using a microrheometer Rheolaser Master and the data expressed as solid–liquid balance (SLB) value, elasticity index (EI), fluidity index (FI) and macroscopic viscosity index (MVI). The dynamic rheological properties were investigated by means of the Kinexus rheometer using a cone-plate geometry. Frequency sweep tests were carried out at 25 °C and 37 °C, between 0.1 Hz and 100 Hz at a strain value within LVR (1%) in order to obtain the storage or elastic modulus (G' “solid like”), loss or viscous modulus (G'' “liquid like”), viscosity and phase angle (tan δ). Zein gels prepared by using 15% and 20% w/v of protein showed a solid-like character, especially at 37°C, as demonstrated by the predominance of the elastic modulus (G’) with respect to the viscous one (G”), a phase angle below 45, high EI and MVI values and a pseudoplastic behavior [1]. Four model compounds, characterized by different physico-chemical characteristics, have been successively entrapped in zein gels. The addition of a water-soluble compounds, such as rhodamine B, promoted a pseudoplastic behavior and a pronounced solid-like characteristic of systems especially when 5% w/w of probe and 20% w/v of biopolymer have been used. As shown in the figure below, Zein gels showed a controlled and prolonged release of the probe; it was interesting to observe that the leakage of rhodamine B was inversely proportional to both the probe and the protein concentration, demonstrating a strong interaction between the compound and the polymeric matrix. The obtained results provide the evidence of the potential use of zein-based gels as films for biomedical and pharmaceutical applications with the aim of modulating the release profiles of several bioactive compounds.

Release profiles of rhodamine B from zein-based gels as a function of time and protein concentration



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P30

The role of conformational entropy in conjugated polymers carbon nanotubes assembly

Rachel Yerushalmi-Rozen[a,b]

[a] Department of Chemical Engneering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

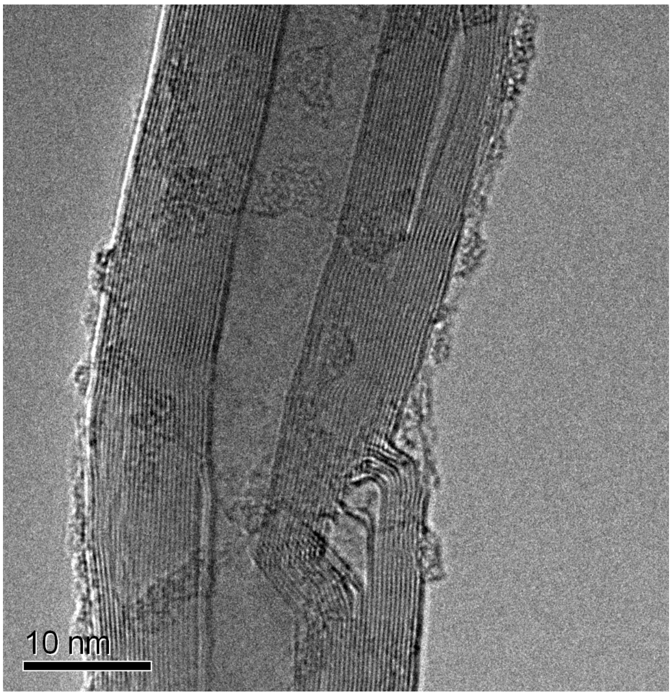
[b] The Ilze Katz Institute for Nanoscience and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

rachely@bgu.ac.il

Abstract

Conjugated polymers can be used for shaping the self-assembly and flow behavior of carbon nanotubes (CNT) in organic solvents. The π-conjugated CNT with their quasi-1D geometry and high curvature are known to form molecular hybrids with the conjugated polymers leading to the formation of nano-structures with structure-dependent photovoltaic properties relevant smart textiles and wearable electronics. While surfactant and polymer mediated dispersions of CNT in aqueous media have been thoroughly investigated and are currently used for processing of CNT into functional materials, CNT processing from organic solvents presents an ongoing challenge. The relatively low solubility of conjugated polymers in the solvents and the non-additive behavior of CNT-polymer hybrids is being explored. In a series of studies, we investigated the formation of molecular hybrids of polythiophenes, poly (3-alkyl thiophenes) P3ATs and carbon nanotubes in a variety of organic solvents. Experimental characterization of the effect of the length of the alkyl side-chains, the regiochemistry of the monomers and the CNTs diameter on the properties of the hybrids, the resulting dispersions and their spinnability via electrospinning was carried out. In addition, molecular simulations were used to rationalize the role of the different parameters on the solution behavior and self-assembly of the polymer-CNT hybrids. Our findings suggest that while the adsorption of the solvated polymer chains onto the CNTs occurs via p-p interactions between the thiophene rings and the CNT surface, and are thus favored by a large conjugation length of the chains, dispersion of CNT depends on the onset of excluded-volume repulsion among the alkyl side-chains of the adsorbed polymers. The latter is dominated by the conformation of the (adsorbed) polymer chains where highly effective excluded volume interactions take place among the alkyl side chains. We describe a few case-studies where the role of the two competing interactions in self-assembly and processability of CNT-P3AT conjugates is detailed. We finally report the utilization of the detailed understanding for developing an approach for electrospinning of optically active fibers, CNT-induced crystallization of P3ATs in thin films, and study of the charge transfer in P3AT-CNT hybrids.

A transmission electron microscopy image of a P3AT-multi-wall carbon nanotube hybrid



List of Authors

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