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Polymers and Additive Manufacturing: From Fundamentals to Applications

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INVITED LECTURES

IL 1

Additive Manufacturing Of Biomedical Polymers For The Development Of Customized Solutions In Regenerative Medicine

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Abstract

Following the pioneering studies carried out in the late nineties, a fast-growing body of literature has been focused on novel additive manufacturing (AM) approaches for the development of polymeric porous implants designed for biomedical applications, such as tissue engineering scaffolds and cranioplasty prostheses. In addition, AM techniques have been combined with other polymer processing techniques, such as freeze drying and particulate leaching, to endow the resulting implant with a multilevel pore arrangement tailored to promote tissue regeneration processes and enhance material/tissue integration. Our research group activity in this area has led to the integration of AM and wet-spinning as a novel hybrid fabrication approach based on the computer-controlled deposition of a coagulating polymeric fiber, extruded directly into a coagulation bath, to build up 3D scaffolds with a layer-by-layer process. The resulting porous structure is characterized by a fully interconnected network of macropores with a size that can be tuned in the range of tens to hundreds of micrometers by varying the fiber lay-down pattern, and a local micro/nanoporous morphology of the polymeric matrix that can be controlled by acting on different parameters of the phase inversion process governing polymer solidification (Figures 1a,b).[1] This multi-scale morphology control represents a powerful tool to tune key scaffold properties strictly related to its porosity, such as biodegradation rate, mechanical behavior, fiber surface roughness, and release kinetics of loaded drugs.

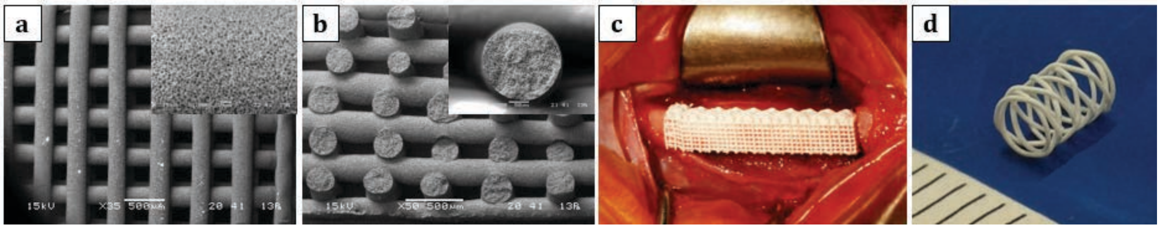

Figure 1. Top view (a) and cross-section (b) scanning electron microscopy micrographs of scaffold by CAWS (scale bar = 500 μm).[1] Photographs of (c) an anatomical scaffold modelled on a critical size (2 cm) defect in a rabbit radius model,[2] and (d) a small caliber intravascular stent (measure unit = 1 mm).

The developed computer-aided wet-spinning (CAWS) technique has been successfully employed to process different biocompatible polymers, either biostable or biodegradable, such as poly(methyl methacrylate), poly(ε-caprolactone), three-arm star poly(ε-caprolactone), poly(3-hydroxybutyrate-*co*-3-hydroxyexanoate), and chitosan/poly(γ-glutamate) polyelectrolyte complexes. Extensive research on personalized solutions in regenerative medicine has led to the development of anatomical polymeric implants starting from 3D digital models, drawn by a CAD software or derived from a computer tomography of an anatomical tissue part (Figure 1c,d). The possibility of directly functionalizing a scaffold during its fabrication, by processing a polymeric solution containing an antibiotic or a bioactive ceramic as solute or suspension, was also recently demonstrated.[3] The expertise gained from these studies has been exploited to develop smart fabrication processes based on a novel machine integrating different AM techniques, whose translation to an industrially-relevant environment is currently under development.

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IL 2

Inorganic Nanostructures Via Sequential Infiltration Synthesis In Self-Assembled Block Copolymer Templates

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Abstract

Sequential infiltration synthesis (SIS) allows the growth of inorganic materials into polymeric films by infiltrating precursors from the gas phase in the polymer template. Combined with the micro phase separated nanostructures resulting from the block copolymer (BCP) self-assembly, SIS elective binds the precursors to only one domain resulting in the formation of an inorganic nanostructure mimicking the original block copolymer template. This strategy provides the opportunity to fabricate inorganic nanostructured surfaces with tunable characteristic dimensions that could find application as hard mask with increased etch resistance for lithographic application. The SIS process using trimethylaluminum (TMA) and H_2O, as metal and oxygen precursors respectively, in self-assembled polystyrene-b-polymethylmethacrylate (PS-*b*-PMMA) BCP films was established as a model system for the formation of Al_2O_3 nanostructures that well reproduce the initial morphology of the PMMA phase. In particular, lamellar or cylinder forming BCP thin films, with nanodomains perpendicularly oriented with respect to the underlying substrate, provide an interesting option for the fabrication of well-ordered and high aspect ratio Al_2O_3 nanostructures. Actually, the thermal stability of the polymeric nanostructures restricts the processing temperature during the infiltration process and consequently the application of the SIS technique is limited to highly reactive metal precursors, such as TMA. In order to expand SIS capabilities and increase the library of inorganic nanostructures that can be fabricated with this technology, the crucial step is the use of more reactive oxidant precursors such as O_3.

In this work, we report an investigation of Al_2O_3 growth in PMMA films by means of dynamic *in situ* spectroscopic ellipsometry. By real time monitoring of the SIS process we unveil the effects of the different competing mechanisms that determine the effective growth of Al_2O_3 in the polymeric film. In particular, swelling of the polymer films is probed by ellipsometry during each SIS cycle, and is affected by the TMA dosing. Two regimes in the SIS process are evidenced, the rate of swelling for cycle is large during the first few cycles, then the increase in the infiltrated polymer thickness for cycle slows down to a value similar to the growth rate of alumina for a standard atomic layer deposition process. Similarly, the resulting alumina film thickness, after removal of the polymeric matrix in oxygen plasma, results growing faster during the first cycles, and then slows down in the following SIS cycles. The investigation of SIS process in poly(styrene-r-methylmethacrylate) random copolymer films with progressively increasing styrene content allows discriminating the roles of the chemisorbed and physisorbed fractions of TMA precursors during the Al_2O_3 growth. Finally, we present a comprehensive morphological (SEM, SE, AFM) and chemical (XPS) characterization of Al_2O_3 nanostructures synthesized using the H_2O and O_3-based SIS processes in self-assembled lamellae and cylinder forming PS-*b*-PMMA thin films. The comparison with the H_2O-based process is used to validate the possibility of using O_3 as oxidant precursor in SIS, thus effectively expanding the range of precursors for the fabrication of inorganic nanostructures.

IL 3

LAYER-BY-LAYER ASSEMBLIES ON PLASTIC FILMS OR FABRICS: CAN SURFACE ENGINEERING PROCESSES MIMIC ADDITIVE MANUFACTURING TECHNIQUES AT A NANO-TO-MICRO SCALE?

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ABSTRACT

So far, the additive manufacturing (AM) techniques developed for plastic materials allowed fulfilling such important goals as no shape limits in manufacturing process, full customisation on the single plastic artefact, localised production and limited waste material. Hence, nowadays it is possible to design the envisaged products not following the constricting conventional manufacturing processes but just focusing on their specific function. However, the AM approach seems to be essentially focused on the macro scale level, because of the thickness of the deposited layers. On the other hand, it could be useful to build up assemblies, with thickness within the nano-to-micro scale. In this context, the Layer-by-Layer (LbL) approach could be very useful. The very first work, describing the principles of this technique, was published in 1966 by Iler [1]. Surprisingly, the potential of the LbL remained hidden till the early 1990s, when Decher and coworkers developed a practical deposition method based on polyanions and polycations [2]. Nowadays, this technique can be tailored to produce nanostructured films, the complex functionality of which can be related to the two following categories: i) tailoring of surface interactions for improving physical and chemical properties: as every object interacts with the environment via its surface, all the properties that depend on this interaction are dictated by the surface functionality; ii) fabricating surface-based functional devices: the sequence used during the deposition defines the final multilayer architecture and thus the device properties.

Basically, LbL consists in an alternate adsorption of chemical species on a chosen substrate exploiting one interaction, which takes place between the selected species, as the driving force for the multilayer build-up. Up to now, most of the multilayer films were fabricated using the electrostatic attraction, although this is not a prerequisite. In fact, there are many others interactions such as donor/acceptor, hydrogen bonding, covalent bonds, stereocomplex formation or specific recognition that have been utilized for the multilayer deposition.

This work is aimed at demonstrating that LbL approach represents a viable AM strategy for obtaining functional architectures at nano-to-micro-scale. Furthermore, some examples [3,4] of assemblies specifically devoted to enhance barrier properties or fire retardancy of the LbL-treated substrates (plastics films or fabrics) will be presented.

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IL 4

Towards New High Performance Radical and Cationic Photoinitiating Systems and Examples in 3D Printing Resins

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Abstract

The field of 3D printing is a hot area and is actually claimed as a “revolution”. The key point in the photopolymerization area is the transformation of multifunctional monomers (*e.g.* acrylates or epoxides) or prepolymers into highly crosslinked networks using a photochemical route where photoinitiating systems PISs generating radical, cation or radical cation initiating species play an important role. This process is widely used in different 3D printing approaches**.** In particular, the use of light emitting diodes (LEDs) to industry processes (such as 3D printing) offers tremendous potential to stimulate industrial renewal.

The state of the art for photopolymerization upon near-UV or visible light will be given. And, new photosensitive formulations (photoinitiating systems and monomers/oligomers) well adapted for 3D (LED) printing and requiring specific conditions (irradiation wavelengths, light intensity, viscosity, writing speed ...) will be presented. All the active component of the photosensitive resins must be developed for this specific application: both the initiating systems and the monomers/oligomers must be taken into account.

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[2] Assi Al Mousawi, Cyril Poriel, Frédéric Dumur, Joumana Toufaily, Tayssir Hamieh, Jean Pierre Fouassier, Jacques Lalevée *Zinc Tetraphenylporphyrin as High Performance Visible Light Photoinitiator of Cationic Photosensitive Resins for LED Projector 3D Printing Applications*, Macromolecules, 2017, 50 (3), 746–753.

IL 5

UHMWPE sintering mechanisms for coating developments by cold-spray

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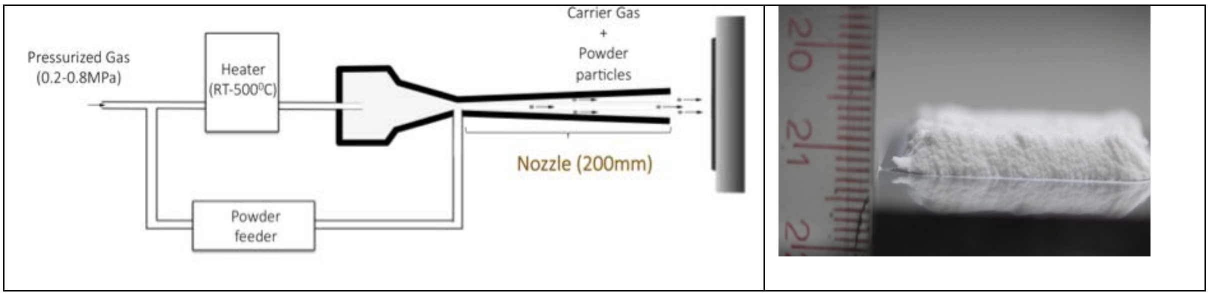
Abstract

Due to extremely high viscosity, UHMWPE (Ultra High Molecular Weight polyethylene) is processed via a method inspired from powder metallurgy: sintering. The kinetic of re-entanglement at the particles interfaces appears to be less time sensitive than temperature sensitive, giving evidence that chain interdiffusion is not governed by a reptation process. The entropy-driven melting explosion is suggested to be the main mechanism of the fast chain re-entanglement in the case of a nascent powder consisting of non-equilibrium chain-disentangled crystals. Another major aspect is the demonstration of the huge co-crystallization efficiency in the interface consolidation in the solid state that hides the kinetics of chain intertwining occurring in the melt. As a consequence UHMWPE, can be sintered in relatively short time if the temperature is high enough. In addition, this material is known for its high impact resistance. We have shown recently that its resistance to hydrodynamic cavitation erosion is excellent. A sintered UHMWPE with molecular weight of 10.5 Mg/mol has shown an exceptional resistance to hydrodynamique cavitation erosion superior to that of stainless steel A2205 or Nickel Aluminum Bronze alloy (in term of erosion depth). Following these results, in the aim to protect marine propellers from hydrodynamic cavitation erosion, which consist in non-planar surfaces, a conventional cold spray machine has been tested (see figure). After slight modifications of this device, and when adding to the UHMWPE powder a slight amount of fumed nano-alumina, coatings of 1-4 mm thickness on both Al and polypropylene substrates have been obtained. These results are consistent with the fact that even if the sintering time is very short in the case of a cold-spray process, a compact coating can be obtained. However, the mechanical properties of these coatings are weaker than that of the sintered material. Additionally, to be able to better understand and improve the adhesion of the powder on a metallic substrate, a specific study has been realized. It has been possible to evaluate the speed and the temperature of a single particle when impacting the substrate in relation with the cold-spray parameters. All these results give the way to improve both the adhesion and the quality of the obtained UHMWPE coatings.



(a) (b)

Figure : (a) cold-spray device, (b) first result of deposition

IL 6

New Polymeric Composite Materials For Additive Layer Manufacturing: An Overview Of Recent Industrial Applications

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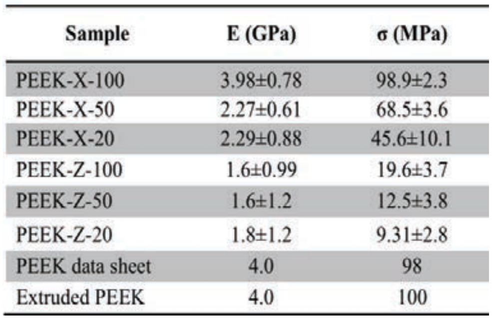
Abstract

Polymeric Additive Layer Manufacturing (ALM) is extensively growing in many industrial applications in addition to rapid prototyping, due to its number of appealing features as intrinsic versatility, freedom of design, realization of lighter structures, to cite a few. Despite a variety of different processing techniques are available on the market (fused deposition modelling (FDM), selective laser sintering (SLS), stereolithography (SLA), etc.), the offered materials are limited and, usually very expensive. This limits the spreading of the techniques in industrial application, despite great interest is recorded. In this work some case studies concerning the use of new polymer based materials for FDM are presented in view of industrial applications. All the manufacturing process, from the formulation of the materials, the filament manufacturing, the optimization of the component design and the setting of the printing process will be discussed and the crucial points will be addressed (Table1). In particular, it will point out if and how the properties of the material (in terms of microstructure, thermal properties, etc.) prior to printing and the resulting properties of printed parts differ, depending on the printing process.

Table 1 Influence of direction of printing and infill on mechanical properties of FDM- PEEK samples



Sample	E (GPa)	σ (MPa)
PEEK-X-100	3.98±0.78	98.9±2.3
PEEK-X-50	2.27±0.61	68.5±3.6
PEEK-X-20	2.29±0.88	45.6±10.1
PEEK-Z-100	1.6±0.99	19.6±3.7
PEEK-Z-50	1.6±1.2	12.5±3.8
PEEK-Z-20	1.8±1.2	9.31±2.8
PEEK data sheet	4.0	98
Extruded PEEK	4.0	100

At first material innovation for space applications is considered: composite and nanocomposite materials based on PEEK or PEI or EPDM or POM matrix reinforced with carbonaceous fillers and nanofillers processed via FDM are presented. Those matrices, in fact, are suitable for space applications. The results show that impressive increments of elastic modulus and/or strength resistance can be obtained, particularly when multiple fillers are used. Moreover, in some cases, other physical properties (as thermal conductivity) can be tuned to fulfil thermomechanical design. The case study of a FDM printed nanosatellite is presented. A brief consideration about recyclability of FDM part will be presented in view of in-space manufacturing.
Successively, a case-study on energy absorbing structures will be addressed. In this case, the use of multiple materials, both based on the use of polymers and polymer nanocomposite, is proposed and it will be point out that an optimum mechanical design can be made possible only if ALM processing is considered.

IL 7

Polymer Physics Of Materials Extrusion 3d Printing

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Abstract

Additive manufacturing (AM) is an important and disruptive production method. In traditional manufacturing techniques customized tooling for a given part requires a large initial investment which is offset by large volume production. In AM no tooling investment is needed and per unit productions costs are flat, which is a huge boon for individualized production. This is especially important in the medical industry where many devices are custom designed for the individual. Although interest in AM seems recent, development has been ongoing for several decades. AM is now at a point where research and development can focus on understanding and improving the process at a fundamental level.

In polymer extrusion 3D printing, a material extrusion AM method, thermoplastic filament is extruded though a rastering nozzle onto previously deposited layers. The resulting strength of the 3D produced part is limited by the strength of the weld between each layer. While numerous factors can affect the weld strength, the temperature of the interface between layers dictates the amount of interdiffusion and entanglement, and thus the weld strength. Experiment, theory, and simulation have found the weld strength in symmetric linear polymer systems scales with $t \sim 0.25$, where t is the isothermal welding time, before plateauing to the bulk strength. Determining this relationship for polymer extrusion 3D printing is the first step to understanding the polymer physics of weld formation in this unique process. However, the weld formation in polymer extrusion is highly non-isothermal and requires calculating an equivalent isothermal welding time to make appropriate comparisons between printing conditions. Equivalent isothermal welding time was determined using a combination of in situ infrared thermography and horizontal shift factors from offline rheological measurements of the neat polymer. Weld strength was measured directly by mode III fracture using a simplified geometry limiting the measurement to a single weld. Since the processing conditions are known a prioi this approach provides the data needed to estimate the final build strength at time of design. The resulting agreement between weld time and weld strength for a range of printing conditions and thermoplastics are discussed.

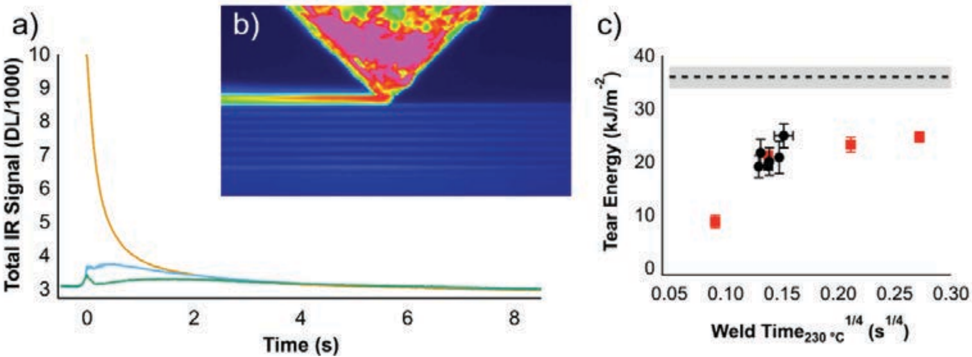

Figure 1 a) Total infrared (IR) signal from printed layer (orange), first sublayer (blue), and second sublayer (green). b) False color IR image of polymer extrusion process. c) Tear energy for various weld times based on polymer extrusion processing conditions.

IL 8

Polymers for laser sintering: from powder to product

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Abstract

Selective laser sintering of polymers is an important added manufacturing technique relying on the deposition of a powder layer that is subsequently sintered together based on a digital representation of the desired shape. Despite of its flexibility, the availability of sinterable polymers is still rather limited since most of the polymeric sinter market is dominated by polyamide-based polymers. Hence, a devoted screening methodology to investigate the sinter potential of new materials is highly wellcome in this field. In this presentation, a 'unit operations' approach is discussed in which the sinterprocess is divided into the relevant subprocesses (see figure 1). For each of the subsections, different experiments have been developed. In the case of polymer powder flow for instance, a newly designed powder spreader rheometer has been designed that allows to mimick the deposition of a powder layer in a sinter station. Moreover, the setup allows to investigate the influence of temperature on the powder rheology which is an important assett in determining the powder bed temperature in an industrial setup. A second new setup is a dilatometer allowing to obtain V-T data at atmospheric conditions. Moreover, this new dilatometer allows heating into the molten state and cooling from the molten state without the applications of pressure which is an important feature in order to assess the shrinkage of the polymer upon cooling from the melt.

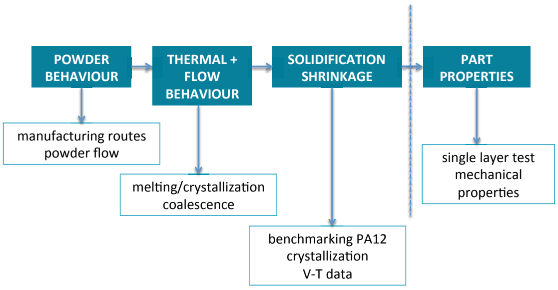

Figure 1: 'unit operations' approach to screen polymers for laser sintering.

Next to presenting the unit operation approach in general and the newly designed experimental tools in particular, the utility of this approach will be demonstrated by means of a few case-studies. It will be shown that the complementary character of the different experimental results can serve as a guideline to select polymers for the process. In addition, the experiments can also help in choosing appropriate processing parameters such as for instance bed temperature in industrial sinter stations.

IL 9

Viscoelastic Modelling Of Gas Pore Collapse During Polymer Sintering

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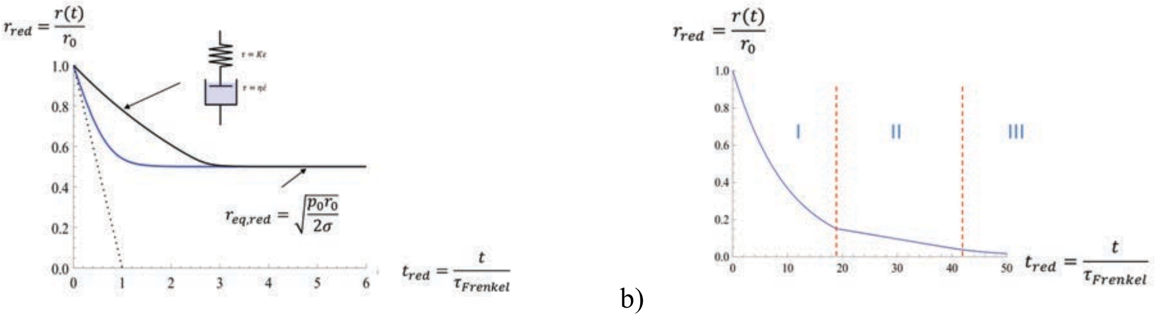
Abstract

Based on Frenkel's Newtonian viscous flow approach [1] and Mackenzie and Shuttleworth's extension accounting for trapped gas [2], a model for the shrinkage of a gas pore in a viscoelastic polymer melt driven by surface tension was developed. The viscoelastic flow of the polymer matrix was described by using a simple viscoelastic model developed by Bellehumeur [3]. In a numerical simulation, the viscoelastic relaxation leads to a pronounced increase of the characteristic time of shrinkage (Fig. 1a), but does not alter the (reduced) final equilibrium gas sphere diameter, $r_{\mathrm{eq,red}}$, which is related to the initial gas pressure p_0, the initial pore radius r_0 and the surface tension of the matrix polymer σ. The reduced pore radius, $r_{\mathrm{red}} = r/r_0$, is plotted in Fig 1a as a function of the reduced time, $t_{\mathrm{red}} = t/\tau_{\mathrm{Frenkel}}$, where τ_{Frenkel}, is the characteristic time for the pore collapse in Frenkel's Newtonian viscous flow approach. The dotted line represents the Frenkel prediction, the blue one the Mackenzie and Shuttleworth one and the black one the model presented here. A first attempt at including gas diffusion into the polymer melt motivated by the works of Kontopoulou and Vlachopoulos [4] and Gogos [5] is shown in Fig. 1b. Numerical solutions of our simplified model [6] show that gas diffusion leads to a complete collapse of the pore and that the rate of diffusion can change the collapse mechanism and the time-dependence of pore radius tremendously. Three characteristic regimes are indicated: Surface tension-driven shrinkage (I), diffusion-controlled shrinkage (II) and final pore collapse (III).



a) b)

Figure 1: Examples for the simulation of the reduced pore radius without gas diffusion (a) and with gas diffusion (b) as a function of the reduced time (for the parameters see [6]).

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IL 10

Advanced Manufacturing for Space Application

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Abstract

NOT PROVIDED

IL 11

Freeformer Technology, optimization of processing parameters

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Abstract

Freeformer from Arburg offers a new technology for additive manufacturing of polymers that enables to use standard pellets as raw material and gives new opportunities to manufacture parts of high quality thanks to its nozzle technology. The main advantage is the possibility to use any material commercially available. However, if printing with qualified materials (ABS, TPU, supporting material, PS) is as easy as inkjet printing, the process has to be optimized before getting parts of good quality in other cases. In the same way that for regular polymer processing technologies like injection molding, optimization of the processing parameters and the choice of appropriate grade is needed. The Freeformer technology is based on two injection molding units that enables to melt the standard granulate and to feed the printing head. The discharge unit featuring a pulsed nozzle closure generates small (down to 200 μm) molten polymer droplets to build, layer- by-layer, three-dimensional parts. Thanks to the presence of two discharge units, parts of complex geometries using water soluble supporting material or parts combining hard and soft materials are easily feasible. Influence of the processing parameters on the microstructure (using SEM, figure 1a and b) of the samples will be presented and its influence on resulting properties (mechanical properties, dimensional accuracy, surface roughness,…) will be illustrated in the case of ABS. The influence of the type of material on the resulting properties of the parts after process optimization will be demonstrated by comparing ABS with other materials like polyolefins, SEBS, EVA,… In the case of soft materials comparison with injection molding will confirm that Freeformer technology is able to manufacture parts with mechanical properties as good as injected parts and even better.

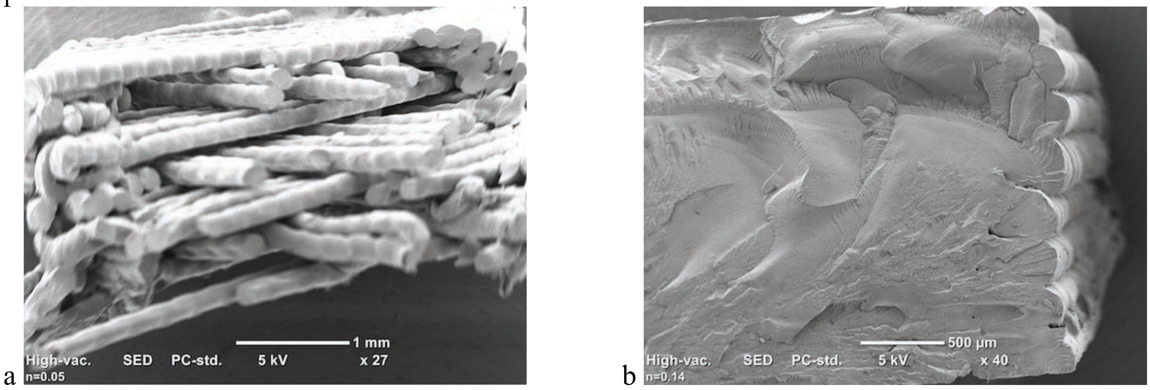

Figure 1. Influence of the discharge number (n, volume of deposited droplets) on the microstructure of parts manufactured using Freeformer technology : (a) n= 0.05 (b) n= à.14

IL 12

Electrically Conductive Filaments And Simulation Tools For 3D Printing

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Abstract

The European Space Agency has set as long term objectives to establish a base on the Moon and later on Mars. The concept involves the utilization of additive manufacturing technologies, so that the parts needed can be manufactured in situ, from an array available materials, either local or brought from from Earth. 3D printing is particularly attractive for this purpose, but materials should be available as filaments. Within this context, the objective of this work is to prepare filaments suitable for 3D printing made from a thermoplastic material with good mechanical properties, high service temperature, electrically conductive and with good surface quality. Availability should be in the kg scale. A hybrid polyetheretherketone (PEEK) / carbon nanotubes (CNT) / graphene nanoplates (GnP) nanocomposite system was selected for this purpose, together with a melt mixing approach for its preparation. The compositions and processing conditions that yielded higher composite electrical conductivity were selected. The filament processing was optimized, the filaments produced were characterized and tested for 3D printing. The printed parts were characterized by tensile testing, electrical conductivity, optical and electron microscopy. A successful outcome was reached, although deposition techniques should be optimized when aiming at conductivity.

The second part of the presentation discusses an analytical solution to the transient heat conduction developing during filament deposition, which is coupled to a routine that activates or deactivates all relevant local boundary conditions depending on part geometry, operating conditions and deposition strategy. Boundary conditions include contact between filament segments, between filament segments and the support, as well as heat transfer with the environment. The resulting MatLab code comprises an adhesion criterion that is used to estimate whether contiguous filament segments will adhere adequately to each other prior to solidification. Computed and experimental data for the filament surface temperature showed very good agreement. Also, adhesion predictions were in accordance with the results of real peel-like tests. The practical potential of this calculation tool is demonstrated by an application example.

ORAL CONTRIBUTIONS

OC1

3D Printing of thermoplastic hierarchical foams

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Abstract

Hierarchical porous structures assume a crucial role in many different fields, thanks to the unusual features deriving from the multi-scale features. The observation of such structures in nature (e.g. seaweeds, bamboo, bone, etc.) has inspired researches to reproduce and exploit these geometrical characteristics. Different processing methods have been developed to process polymers in this direction, with alternative results. It has been previously demonstrated how an Additive Manufacturing process could be exploited to create complex 3D geometries with an hierarchical porous structure[1], but a fine control of the micro-porosity and resolution was still a limit.

We developed a new additive process that allows the deposition of micro-cellular polymeric foams into hierarchical structures in a layer-by-layer fashion, without material modification needed. The control over the deposition of the micro-cellular layers allows a live fine-tuning of pore size and foam morphology, creating a 3D porosity gradient in each desired direction (x,y,z).

Different thermoplastics materials have been successfully processed into micro-cellular layers, as Poly-lactide acids (PLA, PLLA, PLDA), Polycaprolactone (PCL), Poly-lactide-co-caprolactone (PLAPCL), reinforced Poly-lactide-βtricalcium phosphate (PLAβTCP), Poly-lactide-co-glycolide (PLA/PEG), Acrylonitrile butadiene styrene (ABS) and Thermoplastic polyurethane (TPU).

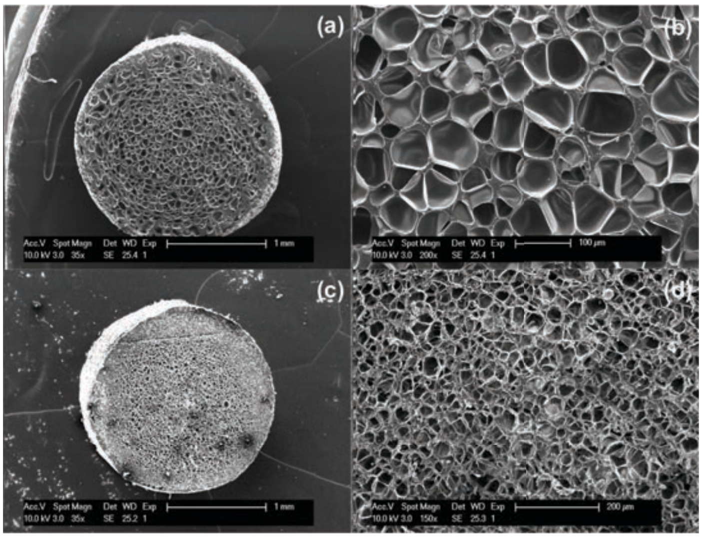

Figure 1: Example of pore morphology in two micro-cellular layers. (a, b) closed porosity of a Poly-lactide-co-caprolactone (PLAPCL) and (c, d) open/closed porosity of a Poly-lactide-βtricalcium phosphate (PLAβTCP).

Conclusion

The process here presented is a newly patented method that introduces a new additive manufacturing method to produce mold-less hierarchical cellular foams, with a continuous control over pore size, foam morphology and overall porosity. Applications involved are namely, but not exclusively, tissue engineering, filtration devices and vibration damping materials.

Acknowledgements

The work was supported by the Swiss National Science Foundation (grant 00021_150190). SEM images were taken thanks to the Interdisciplinary Center for Electron Microscopy (CIME) at EPFL.

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OC2

LAYER BY LAYER PHOTOPOLYMERISATION OF MULTIFUNCTIONAL THIOL/ALKENE BASED HIGH INTERNAL PHASE EMULSIONS

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Abstract

By applying an emulsion templating approach, whereby the continuous phase contains monomers and the droplet phase is used to template primary level pores, a hierarchically porous polymeric material with a cellular interconnected topology with pore hierarchy can be obtained (1). Tipically, a high volume fraction of the droplet phase is used (75% or more) to achieve good interconnectivity of the droplet phase templated primary pores. Such emulsion templating approach was combined with additive manufacturing technology (AMT) where emulsion was prepared in a manner that porosity and viscosity were appropriate for the AMT process and photocuring of emulsions containing a tetrafunctional thiol (pentaerythritoltetrakis 3-mercaptopropionate) and a trifunctional acrylate (trimethylolpropane triacrylate) resulted in a solid object with predetermined three dimensional shape and the internal cellular topology tipical of a polyHIPE material. (2). Figure shows scanning electron image of the internal topology of the object (overall 96% porosity).

Figure

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OC3

SHAREBOT 3D printing Technology

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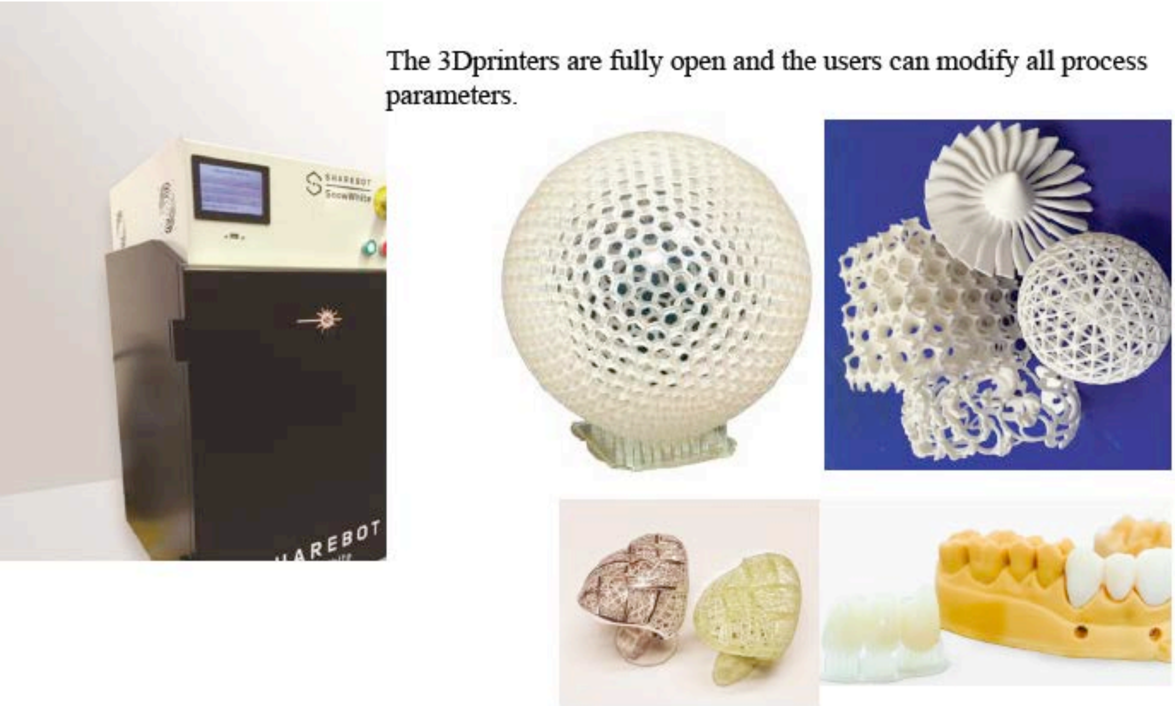
Sharebot is a 3Dprinter producer in different technologies including, FFF, SLS, DLP and SLA.



The 3Dprinters are fully open and the users can modify all process parameters.

Sharebot SnowWhite, **professional desktop SLS 3D printer, some print in DLP and SLA technology**

In the presentation, the technical features of the 3Dprinters will be described with special regard to the possibility to adjust parameters in order to test novel materials and optimize the process conditions.

A couple of case history will be also described relevant to the use of a PA12 based material and a biocompatible material. Finally, our strategy to improve the quality of our products by establishing collaborations with Academic or research structures will be delineated.

OC 4

Novel method to synthesise tuneable polyionic materials by post-polymerisation for inkjet printing applications

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Abstract

In this contribution, our efforts to develop a novel method to 3D print multi-functional materials will be presented. Polymeric materials functionalised with analogous units to ionic liquids have been synthesised and characterised and their physico-chemical properties established. Applications for inkjet and stereolithography have been developed.

Ionic liquids are salts with melting point below 100 °C and usually below room temperature.[1] The virtually unlimited number of combinations anion-cation gives rise to a plethora of interesting properties that have found applications across numerous fields, including catalysis,[2] energy as electrolytes [3] and separation[4] to mention just a few. However, the high cost and technical limitations, like high viscosity hinders their widespread application. One solution to these problems consists on creating solid supports of organic or inorganic nature that contain analogous phases to ionic liquids supported via ionic or covalent bonds.[5] The effective transfer of properties from the bulk liquid phase to the support allows taking advantage of the properties of ionic liquids, while minimising cost and potential negative effects.[6] Coupling the molecular functionality of IL-like based materials with the freedom of design from additive manufacturing represent a very attractive approach to develop innovative applications.

The requirements of viscosity and surface tension for inkjet are a limiting factor to develop a universal protocol to process polymerisable ionic liquid, typically too viscous for this type of application. Herein, a new method will be presented, where polymeric materials for inkjetting with tuneable mechanical properties, hydrophilic/hydrophobic balance and able to stabilise nanostructured materials. A baseline formulation is printed and photopolymerised and subsequently quaternised employing different routes. Further fine tuning of the material properties is demonstrated by anion methatesis on the films.

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OC5

Development Of DLP-3D Printable Functional Materials

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Abstract

In recent years, three-dimensional (3D) printing technology has rapidly grown, showing great potentialities that make it suitable for a variety of application fields: from biomedicine to electronics and even further.[1-3] The research here presented is placed in this frame and it is focused on materials for printing technologies based on solidification upon exposure to a light source, and, in particular, for digital light processing (DLP).

With such a technique, it is possible to tailor the final properties of the printed object by choosing the right components of the reactive liquid formulations. A large variety of systems can be conceived for the production of structures with advanced properties and functions; the good balance between final properties and printability has to be found for every system.

Different strategies can be followed ranging from the use of common reinforcing filler (e.g. carbon nanotubes)[4], to the addition of liquid precursors of the reinforcing phase that enable the in situ generation of the filler into the printed parts.[5] The choice of the right components brings the desired functionalities, enabling the production of intrinsically functional objects. Following this idea, a soluble silver precursor can be exploited to in situ generate nanoparticles to obtain object with enhanced conductivity[6] or the addition of suitable functional agents can enable the immobilization of biomolecules on 3D printed structures that can be used as biosensors.

These studies open the possibility of developing functional objects with complex geometries through a simple but very precise process.

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OC6

Ultimate Eco-Resin For Sustainable Additive Manufacturing

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Abstract

As techniques such as 3d printing evolve from the domain of prototyping towards direct digital manufacturing, issues such as sustainability of the materials used become more critical. In this work we report and analyse the results of the use of rosin as a material for use in additive manufacturing. This forms part of the FAVAM project at the Centre for Rapid and Sustainable Product Development which seeks to add economic value to products from forests in order to help stabilise rural communities and maintain biodiversity. Rosin is thermoplastic resin based on a mixture of acids principally abietic acid. It is obtained from resin tapped from pine trees. The resin is a mixture of rosin, turpentine and water. The extraction process is very eco friendly consuming little energy and producing only water as waste. In previous work we have developed an micro-extruder based fused deposition modelling system and we have utilised this to explore the potential of rosin based resins for additive manufacturing. As the extruder-based system can used small pieces of polymer as the raw material, it provides a convenient laboratory system for exploring material systems with differing compositions. The extruder-based system has a number of system based parameters which need to be optimised for a particular material, these include the melt temperature, the extrusion speed, the extrusion nozzle diameter as well as the deposition system. Equally for any particular material system, there are material parameters which need to be matched. We have systematically explored the Rosin system with various additives including polymers, and biopolymer-based reinforcing fillers. We have prepared specific 3-d geometrical shapes using these materials in conjunction with the extruder based system. We used 3-d scanning techniques to evaluate the precision of the 3-d process against the specification in the digital definition and to identify particular issues in terms of finish and resolution.

We find that although objects could be produced the shape definition was unsatisfactory and we conclude that the rosin alone does not have suitable visco-elastic properties to be used in the extruder-based additive manufacturing process. We have explored a number of modification routes. We find that the addition of poly(ε-caprolactone), a biodegradable polymer, to the rosin serves to substantially modify the visco-elastic properties and leads to the production of high quality objects. We have also examined the possibility of using nanoclay and reinforcing fillers obtained from forest products for this purpose. We compare the properties of the final products and the suitability of the composites for additive manufacturing.

We show that by shortening the material process route from the forest to the final products we can reduce greatly the energy inputs and the quantity of waste and thus improve the sustainability of the material system close to the ultimate which can be attained.

This research was supported by the FCT (Portugal) through Strategic Project - UI 4044.

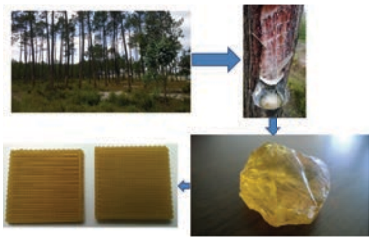

Figure: The stages of producing rosin for use in additive manufacturing of scaffolds for tissue engineering

OC7

Novel Polypropylene/Additives with High Thermal/Oxidative Stability; Synthesis and Applications

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Abstract

Despite huge commercial success, polypropylene (PP) is not suitable for the applications that require high temperature operational conditions (>80 °C), due to the combination of chemical and physical instability. Recently, we have developed a new family of PP/additive materials that show exceptional high thermal and oxidative stability.

These materials are suitable for high temperature applications with constant theating at >110 °C for long period of time. The key additive is based on a polypropylene copolymer (PP-HP) containing some specific pendant hindered phenol (antioxidant) groups in the side chains. This PP-HP copolymer can form co-crystallization with matrix. The resulting PP products show significantly higher thermal-oxidative stability than the commercial PP products that contain various antioxidants and stabilizers. In addition to the diffusion and/or extraction (particularly acute in films and coatings), the PP-bonded HP moieties exhibit a unique crosslinking reaction feature between PP polymer chains by cycloaddition reaction in forming a PP network.

In other words, instead of PP chain degradation upon thermal/oxidation reaction happened under high temperature conditions, the PP-HP polymer chains form a PP network with increasing strength and stability.

OC8

PRODUCTION AND QUALIFICATION OF POLYMER POWDERS FOR APPLICATION IN LASER SINTERING

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Abstract

Millions of tons of polymer powders are used in industrial applications as diverse as furniture, automotive, electronic, public transport, medicine, textile, cosmetic and others. Several technologies are established to serve the needs and produce appropriate powders for these markets. In the case of Additive Manufacturing, Laser Sintering (LS) is based on polymer powders too. It is well known that powders manufactured with the “traditional technologies” match poorly to LS. In most cases the primary basic feature, the powder size distribution (PSD), is not in the preferred range for LS (20 µm to 80 µm). However, even when the PSD fits well, almost all powders fail in LS due to further processing problems. The appearance of streaks, cracks, caking, uneven surfaces or an insufficient powder bed density are just a few problems which can be cited here. This means that information about PSD-N and PSD-V (PSD with respect to the number and volume distribution) is by far not enough to qualify powders for LS and predict their processing behaviour. It becomes obvious that beside PSD a further qualification of shape and surface characteristics of particles is mandatory.

The presentation describes an approach to qualify single powder particles in a semi-automatic procedure with optical microscopy and a mathematical evaluation. The core value of the calculation is the so-called “elliptic smoothness” (ES). This is the comparison of the contour of a single particle with the contour of a barycentre ellipsis having the same area as the 2D-silhouette of the said particle. ES, as a novel shape factor, gives an impression of the evenness of a particle surface and can be combined with further factors like particle diameter (pd), aspect ratio (ar) and solidity (s) to improve the information about particle shape (Figure 1). After investigation of several research and production LS- powders by applying this approach, an impression becomes clearer how the distributions should look like to be potentially successful in LS-processing.

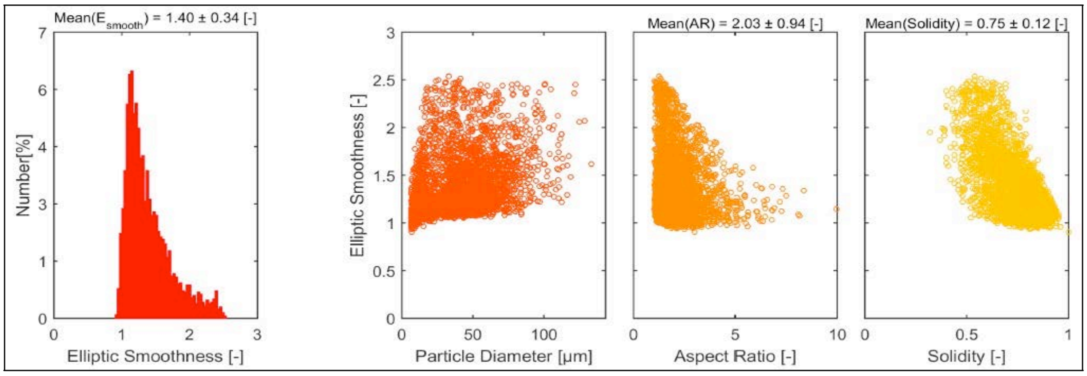

Figure 1: Distribution of elliptic smoothness of a LS research powder in connection with pd, ar and s;

In summary, the presentation issues some options for polymer powder production fitting to LS-technology, addressing the pros and cons of the different methods and focus on the refined qualification procedure for powders and particles. Elliptic smoothness in connection with pd, ar and s will be introduced in order to qualify powders for the LS-technology and gain information on powder processability

OC9

VERSATILE FABRICATION OF POLYMER ELECTROLYTE MEMBRANES FOR FUEL CELLS

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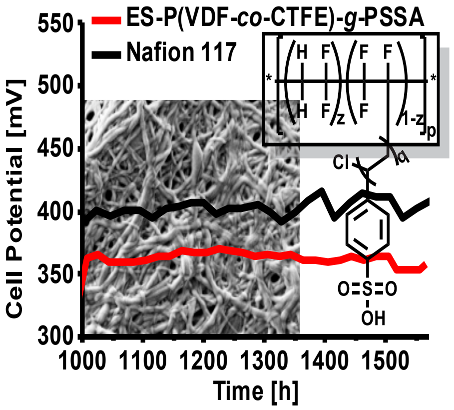
Abstract

Materials for proton exchange membranes often referred to as polymer electrolyte membranes (PEMs) have been intensively researched for more than half a century. PEMs especially aiming for low temperature fuel cell applications as alternative to mobile or stationary energy conversion devices due to its high efficiency and low emission are of immense interest. Nafion®, the DuPont membranes based on perfluorinated polyether with sulfonic acid groups that are employed in many fuel cells is often considered the market leader. However, Nafion suffers several drawbacks since it requires high degree of humidification and has low mechanical strength and conductivity at temperatures above 90ºC, furthermore it is expensive; thus alternatives with improved properties and performance are still in great demand.

We here present our novel PEMs for fuel cell applications that are synthesized by surface-initiated (SI) atom transfer radical polymerization (ATRP). Poly(vinylidene fluoride-*co*-chlorotrifluoro-ethylene) (P(VDF-*co*-CTFE) is electrospun into a 50 µm thick mat, which is then employed as multifunctional initiator for copper-mediated SI ATRP of 4-styrene sulfonic acid sodium salt. Fine-tuning of the ATRP conditions allows adjustment of the membrane's ion exchange capacity by varying the loading of the grafted ionomer. The structure and composition of the membranes are investigated by spectroscopic means and thermogravimetric analysis, respectively. The membrane morphology is probed by scanning electron microscopy. A membrane with proton conductivity as high as 100 mS cm^{-1} is obtained. A long-term durability study in direct methanol fuel cells is conducted for over 1500 h demonstrating the viability of this novel facile approach. Thus our alternative is simple to produce and have fuel cell performance similar to Nafion.



Long-term durability tests for direct methanol fuel cells: Membrane electrode assemblies with Nafion 117 and electrospun P(VDF-*co*-CTFE)-*g*-PSSA.
Current density: 18.6 mA cm^{-2}.

OC10

POLYVINYL ALCOHOL REINFORCED CRYSTALLINE NANOCELLULOSE IN 3D PRINTING APPLICATION

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Abstract

Climate change and ecological catastrophes are pushing strongly the research to find solutions to preserve our environment, especially in the field of processing raw materials and in the industrial manufacturing. The widespread of new technologies like 3D printing give us the possibility to produce an object where it is really required. This could lead to a reduction in CO_2 emissions due to the less transportation needed [1]. The development of sustainable and degradable polymers is the natural step to improve the "green" benefits of 3D printing. Poly vinyl alcohol (PVOH) is recognized as one of the very few vinyl polymers soluble in water also susceptible of ultimate biodegradation[2], but for its poor mechanical properties PVOH is used in just few applications.

The aim of this work is to produce biodegradable polyvinyl alcohol reinforced with cellulose nanocrystals (CNC) nanocomposites filaments to improve the thermo-mechanical performance in 3D printing fused deposition modeling (FDM).

Cellulose nanocrystals in water solution were prepared from micro-cellulose through a sulfuric acid hydrolysis [3]. Nanocomposites of PVOH containing various amounts of CNC produced by solution mixing and grinded to obtain filaments through a single screw extruder. Dumbbell specimens were printed with the aid of a 3D printer.

CNC particles appear homogeneously dispersed without noticeable aggregates and no phase separation had taken place during the extrusion process as we can see from the SEM image (Figure 1). The effect of CNC on thermal properties of PVOH and its composites was evaluated with thermogravimetric analysis. The peak in mass loss for neat PVOH is shifted to higher temperatures, with the increase of filler content, enhancing the thermal stability of the composites as compared with the neat PVOH. A progressive enhancement in the storage (E') modulus as the filler loading increases was observed increasing the amount of nanofiller in the filament and in 3D printed specimens (Figure 2). An increase of 280% in the value of storage modulus at room temperature was reached in 3D samples with a concentration of 10wt%. A reduction of the creep compliance with the increase of filler content confirms an improvement of the dimensional stability. The representative stress-strain curves of examined 3D printed nanocomposites, reported in Figure 3, underline an interesting increase of the stiffness and the strength of PVOH due to the CNC introduction.

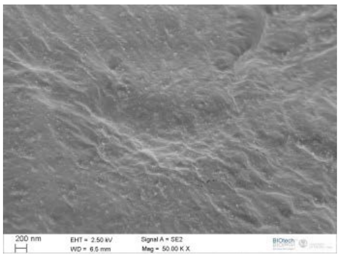

Figure 1. Cryo-fractured surface of PVOH with 10wt% of CN

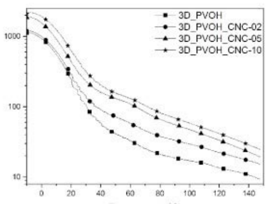

Figure 2. Storage modulus curves for 3D printed samples

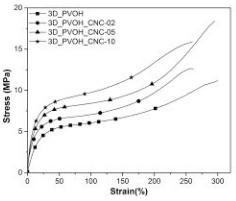

Figure 3. Representative stress – strain curves from tensile test

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OC11

ENGINEERING POLYMERS FOR FUSED DEPOSITION MODELLING: HIGH PERFORMANCES VS "GREEN" LOW COST SOLUTIONS

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Abstract

Fused Deposition Modelling (FDM) is recognized as the best additive manufacturing technique when functional parts are required. FDM materials are currently limited to a selected number and type of polymers, which spans from those used in consumer machines (i.e. PLA, ABS, Ny, PETG and PC) to those used in professional equipment (i.e. ABS, PC, Ny, ASA, PPSF and PEI). The results in terms of obtained performances are affected by the printing conditions and, still, some gaps exist compared to injection moulding samples. Moreover, the material development for FDM is still limited. Recently, much emphasis has been drawn by the development of polymer-based composites for FDM[1] but, still, few truly commercially viable solutions are available.

The present paper reports the work carried out in the COMMAND project towards the development of viable thermoplastic filaments to fulfil the requirements for high performance systems or to obtain "green" low cost solutions. The development of high performance systems was pursued by the extrusion of PEEK based filaments[2] (Fig.1). The improvement of PEEK formulation by selectively adding specific additives allowed to develop a commercial grade filaments which has been extensively tested on the Roboze One +400 machine. The PEEK based formulation is intended for niche market applications due to its high cost. However, to overcome the cost issued, other solutions have been investigated based on the use of polymer blends. In addition to that, the research has been focused also on novel formulations based on recycled polymer matrices or low cost PE matrices reinforced with recycled milled carbon fibres. Furthermore, cellulose fiber/poly(vinyl)alcohol composites were investigated as possible composite material for FDM system; novel formulations were set up using different rates of cellulose to ensure easy recycling in water of the biocomposite. These systems showed enhanced mechanical properties compared to neat systems with lower production cost compared to commercial alternatives and with some benefit in terms of environmental impact.

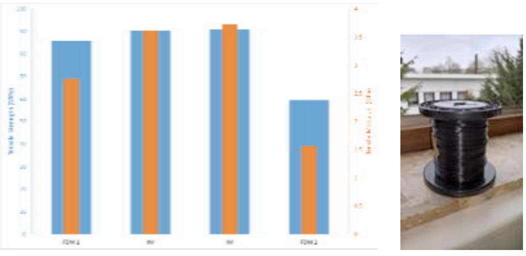

Fig.1 PEEK mechanical properties and PEEK filament spool

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OC12

NUMERICAL CALCULATIONS OF FLOW, DISENTANGLEMENT, AND WELDING DURING FUSED FILAMENT FABRICATION (FFF)

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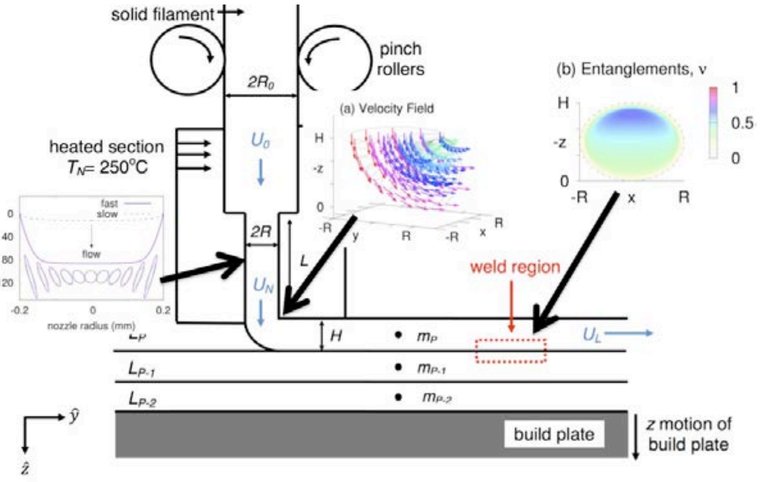
Abstract

Fused filament fabrication (FFF) is proving to be a versatile and convenient method for producing plastic parts via additive manufacturing. Unfortunately, FFF-produced parts often have poor mechanical properties. In addition to voids, the strength of the weld between filaments is not as strong as the bulk material. This is because there is a limited time for polymer welding as the filaments cool below the glass transition to solidify. Here we calculate the flow and orientational properties of FFF filaments using a molecularly-aware constitutive model, the Rolie-Poly model for polymer melts, as a paradigm for understanding FFF in glass-forming polymers page[1]. Semicrystalline (e.g. PLA) or composite polymers (e.g. ABS), whose rheologies and solidification are much more complex, do not yet possess adequate constitutive models. We find that the flow within the nozzle induces a skin layer of molten polymer that is oriented, stretched, and partially entangled with respect to the equilibrium polymer. Upon exiting the nozzle and turning the sharp corner the polymer suffers significantly more stretch and orientation, and much greater disentanglement in the skin layer. The resulting filament has an anisotropic cross section and inhomogeneous orientation. We then use the as-deposited properties, together with the cooling rate calibrated from experimental measurements, to estimate the degree of polymer welding before solidification, and thus the weld strength. We study the weld strength as a function of entanglement number, printing speed, and temperature, and provide some design criteria[2].



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[1] C McIlroy and PD Olmsted, "Deformation of an Amorphous Polymer during the Fused-Filament-Fabrication Method for Additive Manufacturing", *Journal of Rheology* **61** (2017) 379.

[2] C McIlroy and PD Olmsted, "Disentanglement Effects on the Welding Behaviour of Polymer Melts during the Fused-Filament-Fabrication Method for Additive Manufacturing" (2017) https://arxiv.org/abs/1611.01522.

OC13

NUMERICAL SIMULATION OF HIGH VISCOSITY FLUID EXTRUSION AND MATERIAL DEPOSITION ON THE PRINTING PLATFORM USING TWO PHASE FLOW SIMULATION

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Abstract

Among additive manufacturing (AM) technologies, material extrusion or FFF: Fused Filament Fabrication is widely used for 3D printing of polymers. However, materials used in this process are limited to low melting point thermoplastics, with low mechanical properties, whereas aerospace and high-tech industries require high-performance polymers, in the other word, thermal resistance higher than 200°C in continuous use, elastic modulus higher than the few GPa and low sensitivity to thermo-oxidative ageing. The polymers of the PAEK family are the most durable thermoplastics among the thermoplastics. Nevertheless, printing of high-performance thermoplastics is still a challenge due to its processing temperature close to 400°C and cooling control during the process, to get the highest mechanical strength reachable.

In order to control the quality of the printed parts and the efficiency of the material deposition on the printing platform, the process has been investigated using numerical simulation. The aim is to simulate the phenomenon occurring in the process. The viscous flow of the polymer during deposition is modeled and simulated by considering the heat transfers with phase change. The modeling must take into account the evolution of physical properties of the polymer with temperature up to the solidification on cooling.

The height of the deposited layer and the quality of the manufactured part are dependent on multiple printing parameters such as temperature, material feeding velocity, moving speed of the deposition platform and also the gap between the extrusion nozzle and deposition platform. On the other hand, the material properties (i.e. viscosity) affect the efficiency of the printing process. Numerical simulation has been carried out using two-phase flow simulation to validate coalescence model and the behaviour of the extruded filament.

Primarily, the coalescence for two nearby extrudate has been done using numerical simulation and have been compared to the experimental results. Furthermore, the numerical simulation of the extrudate after exit form nozzle has been done. Validation of the results has been done by experimental observation and bibliographic studies.

The perspective of the current work is dedicated to coupling the heat transfer with the deposition of the material using two phases simulation.

OC14

3D PRINTING OPTIMIZATION OF PLLA BASED ON RHEOLOGICAL ANALYSIS

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The additive manufacturing process, which has experimented a rapid growth during the last decade, is usually defined as the conversion of a computer aided design (CAD) model into a real model through a quick and easy process[1]. The most widespread example of this technology is the 3D printing, which has been already implemented in various applications for the automotive and aerospace industries and also within the medical field. The use of this technology has gained great importance in recent years, and around of this it has generated different modes of printing. The different types of 3d printings depend on the mode in which the printing is performed. In the present work we carried out a 3D impression by deposition of the melted material (FDM) layer by layer.

For appropriate use of the 3D printing it is necessary to study the rheological and thermal behavior of polymers. The parameters involved in the process of printing must be controlled in order to guarantee the correct performance of the printed product. Printing have to be performed within very strict ranges of temperature, printing rate and pressure; otherwise good adhesion between layers will not be achieved, being this fact of paramount importance. Although a great effort has been made to describe practical applications through empiric experience, the literature concerning the physical basis of the printing of polymers remains to date limited[2], so that selecting good printing conditions could become a complex and laborious task.

Therefore, for a proper use of the 3D printing it is essential to know the variables that affect the welding process or adhesion of the layers that conform the final product. In order for the adhesion between layers to be adequate, it is necessary to undergo a process of diffusion between the polymer chains of the different layers. The welding process occurs in the terminal or flow zone, where the diffusion takes place, between one layer of the polymer and another, and strongly depends on the temperature and the time of contact between the layers, which are at the same time dependent on the structure of the polymer and molecular weight.

In this work the dynamic viscoelasticity of three L-lactides with different molecular weights has been analyzed in order to determine the frequency and temperature limits of the terminal zone. This will enable to determine which materials are suitable for their use in a 3D printer and the recommended conditions in terms of the range of velocity and temperature parameters. Accordingly, it will be possible to estimate printing conditions a priori in order to enhance the process of printing and improve the quality of the obtained printed products.

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OC15

POROSITY DISSOLUTION IN SLS (SELECTIVE LASER SINTERING) PROCESS

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Abstract

The polymer grains coalesce faster at surface than deeper in the powder bed because of higher laser radiation absorption at powder surface. Then air porosities are embedded in the melted polymer layer, whose thickness can reach a few hundred microns. Due to the pressure induced by polymer surface tension around the bubble, air slowly diffuses through polymer melt allowing porosities to dissolve if their size is small enough and the time long enough. To simulate bubble dissolution in rotomolding process, Kontopoulos et al. [1] determined the kinetic of bubble shrinking by coupling air diffusion and polymer flow in an infinite medium. Later, Gogos[2] considered only the diffusion phenomenon and showed that air diffusion drastically depends on initial conditions, i.e. air content in the polymer compared to air saturation content.

Knowing that porosities in melted polymer are close to the surface of powder bed in SLS process, it is no more possible to considerate an infinite medium. Therefore, to assess porosity resorption kinetic, we considered the dissolution of an air porosity embedded in melted polymer sphere. The melted polymer was considered as Newtonian and gas diffusion was supposed to obey a Fick law. At polymer/gas interface, the concentration of gas in the polymer was supposed to follow Henry Law. The problem was solved in one dimension thanks to a finite element method, flow and diffusion was coupled in an implicit scheme.

We first find that a ratio of about ten between the diameter of the melted polymer sphere and the one of the porosity is equivalent to porosity in an infinite medium. The influence of time of porosity dissolution versus the diameter of porosity, surface tension and diffusion coefficient obeys to a power law. The viscosity has a small and linear influence on time of porosity dissolution, which means that the time scale of diffusion is larger than the one of the flow. We confirm the strong influence of the initial gas concentration found by [1,2] for polymer medium which can be considered as infinite. This influence decreases with the ratio of sphere diameter to porosity diameter. A last, it seems important to take into account the advection in the flow simulation, it decreases significantly the time of porosity dissolution.

Acknowledgments:
The work was done in the framework of 3D-SLS project "3D-numerical Simulation of the Laser Sintering processing of thermoplastic powders for the prediction of microstructural features and part warpage" coordinated by Dr Claire Barres (IMP, INSA Lyon). This project is financed from funds of the French national research agency (ANR).

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OC16

FUNDAMENTAL APPROACHES OF POLYMER POWDER TRANSFORMATION DURING LASER SINTERING

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Abstract

Laser sintering (LS) of polymer powders is one of the main two additive manufacturing (AM) technologies used with thermoplastic polymers. Although acceptable, the mechanical properties of parts remain very anisotropic and inferior to those obtained with traditional processes. Key issues are to improve the mechanical characteristics and the repeatability, reliability and durability of parts made by laser sintering.

Two main axes must be addressed. First, improvements on existing materials and developments of new ones are a necessity. Second, better control on processing must be achieved to enhance the acceptance of LS by industrial end-users. It requires deeper understanding of the mechanisms governing the part building. Especially, the thermal phenomena are not fully understood. This presentation illustrates the experimental and modelling work as well as the numerica simulations which have been developed for several years at our laboratories in order to analyse the influence of process conditions and of material characteristics on the morphologies and properties of parts.

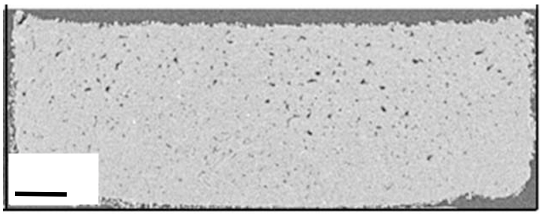

Figure 1 : morphology of a PA12 laser sintered part observed by X-ray tomography [1].

In the LS process the consolidation mechanisms are driven by the coalescence of molten particles and the densification due to gas diffusion in the melt. This results in a more or less porous mesostructure (Figure 1) whose evolution stops upon solidification of the polymer (most often a semi-crystalline polymer). Therefore, the rheological behaviour and the crystallization kinetics of the polymer are key factors in the bonding and consolidation mechanisms [1]. They depend on the thermal conditions through many multiphysics couplings. Computations of the temperature profiles in the layers (Figure 2) allow to follow the evolution of their density [2]. Thus, the results presented here contribute to clarify the impact of processing conditions on the development of the meso- and microstructure of the part and hence on its final properties.

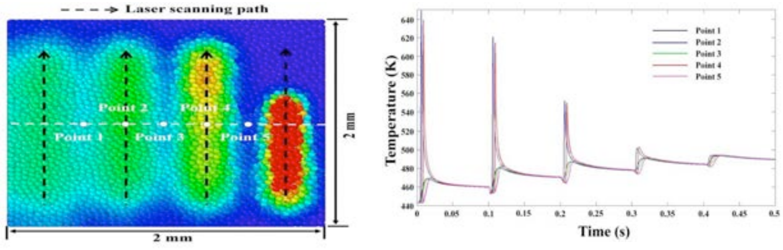

Figure 2 : Temperature field at the surface (left) and evolution vs. time at some points in five successive PA12 powder layers (right) [2].

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OC17

ADDITIVE MANUFACTURING OF HIGH TEMPERATURE NYLONS BY SELECTIVE LASER SINTERING: THERMAL STABILITY AS A KEY CHALLENGE

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Abstract

The production of parts by Additive manufacturing has grown very fast in the past years. Among the available technologies, the Selective Laser Sintering (SLS) of polymers is a good alternative to injection molding to save time and cost of developments. SLS is one of the preferred techniques to produce functional prototypes, small series and spare parts.

Few polymers for SLS are commercially available, among which PA12, PA11 or PP. There powders are mainly used for visual prototypes, but show limitation for applications requiring demanding mechanical and thermal resistance. More recently, PEEK powder has been proposed to the market, however the latter requires a specific SLS machine technology, preventing this material to be used widely at the date. This is why there is today a need for high performance polymers with easy processing.

Solvay has developed understanding of the key challenges for the development of polyamide 6 (PA6) powders for SLS. Due to its higher hydrophilicity and sensitivity to thermooxydation, PA6 cannot be processed by SLS with conditions similar to those of PA12. In addition, the ability of the powder to retain its physical properties is very important to ensure good powder recyclability.

During SLS process, powder is pre-heated for several hours at a temperature between 120°C and 160°C. Close to printing area, the material is submitted to a temperature close to melting point for a shorter time. Laser powder brings the needed energy to melt the powder in selected zone. The present study will focus on the evolution of material properties for various thermal conditions. Since the powder thermal stability plays an important role on the recyclability, the above material properties will be studied for increasing number of SLS productions.

First, the evolution of crystalline phase in the PA powder will be studied thanks to DSC. The correlation between SLS processing window and DSC profile will be reminded. This part will present the melting and crystallization temperatures, crystallinity ratio, crystalline phase, for different thermal conditions during SLS process.

Secondly, the influence of the processing conditions during SLS process on the amorphous phase of PA6 powder will be highlighted. The polymer chain length will be evaluated, and phenomena of postcondensation, hydrolysis and thermooxydative degradation in PA6 powder will be discussed.

Finally, the mechanical properties of printed PA6 parts will be compared to molded PA6 to study the influence of the process. To conclude, this part will present the recommendations for PA6 SLS processing and obtained mechanical performance versus PA12 as a benchmark.

OC18

EVOLUTION OF MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF POLYAMIDE PARTS MANUFACTURED BY SLS REGARDING ANNEALING CONDITIONS.

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Abstract

New Selective Laser Sintering (SLS) machines have come to market since 2014 with reduced sizes and costs in order to enable new end-users to have access to this process with more flexibility regarding materials and processing parameters. Those “lab-scale” machines do not possess however the same temperature control as industrial ones. Thus, the temperature environment and history of the parts made in these two ranges of machines are very different. In industrial SLS machines, the build tank is maintained at high temperature for the duration of the whole fabrication job, i.e. for hours due to the volume of the tank, and the cooling is slow. Hence, the longer the manufacturing batch, the largest the disparities in the thermal history between the first layers and the last ones. Therefore, the “annealing” process of the first layers built is different from the last ones.

In order to understand the impact of thermal history on the structure-properties relationships in PA12 parts made in industrial SLS machines, we used a laboratory machine (Sharebot Snowhite®) to manufacture tensile test samples which were then annealed in different time and temperature conditions under inert atmosphere. The main objective was to link the modifications of the physico-chemical characteristics of the polymer and of its mechanical properties to the thermal conditions endured during processing.

The changes in the microstructural and mechanical features of the polymer after annealing were studied using density measurements, differential scanning calorimetry (DSC), polarized optical microscopy (POM) and tensile tests.

It was observed that annealing has substantial effects on the microstructure and then modifies the mechanical properties as a result of molecular weight and/or crystalline structure changes in polyamide 12.

In summary, this investigation provides an evidence of how appropriate thermal treatments can be used to tune the mechanical properties of SLS PA12 materials and then emphasizes the need for better controlled temperature conditions in SLS machines to improve reproducibility.

OC19

INFLUENCE OF CRISTALLINITY ON MECHANICAL BEHAVIOUR OF PA12 SAMPLES PRODUCED BY SELECTIVE LASER SINTERING

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Abstract

Selective Laser Sintering (SLS) is a widely used additive manufacturing technique in which layers of preheated powder (e.g. PA12, PA11, TPU, etc.) are spread after which laser radiation is used to liquefy and fuse the material at specific locations corresponding to a CAD file of the final part[1]. After this, the build platform with all parts is slowly cooled to room temperature to avoid shrinkage and distortion of the SLS components. Compared with conventional production techniques such as injection moulding, the SLS process offers a number of advantages including short design to manufacturing cycle time, high geometrical freedom, customized components and inexpensive production of small numbers of parts. It is known that the cooling down phase of the SLS process is an important parameter in determining the properties of the SLS fabricated components. It can influence the thermal stresses within the components which can cause uneven shrinkage or even warpage of the components. The crystallinity of the components can also be influenced by the cooling process. Higher cooling rates results in the formation of more amorphous phase while lower cooling rates result in more crystalline phases. This will lead to different mechanical properties of the components. In addition, the density of the fabricated components and the recyclability of the un-sintered powder can also be affected by the cooling process.

To the knowledge of the authors, there is little work being reported on the actual influence of the cooling down step on the mechanical behaviour of SLS fabricated components. This is partly addressed in this work by studying the influence of the cooling down on crystallinity and on resulting quasi-static and fatigue behaviour of SLS-PA12 samples. Crystallinity was measured on samples produced with different cooling rates by X-ray diffraction and by DSC. Quasi-static and fatigue experiments were performed under temperature controlled conditions and all results were compared with data from conventional PA12 samples produced by compression moulding. A clear relation between crystallinity and mechanical performance was established and first steps were made for simulating the cooling down such that this important step in the SLS process chain can be optimised for achieving desired properties.

Acknowledgements: This research was supported by FWO (Fonds wetenschappelijk Onderzoek) Vlaanderen [grant number FWO-12S4615N].

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OC20

AN EXPERIMENTAL INVESTIGATION TO THE ROLE OF PROCESS PARAMETERS FOR SLS OF A TPU POLYMER

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Abstract

This work investigates the role of various process parameters (such as powder bed temperature, laser parameters, and scanning strategies) on the obtainable density, mechanical properties, microstructure, and even dimensional accuracy of a TPU elastomer (coded TPU-SA95 in a recent work[1]). It was shown that despite TPU is not a semi-crystalline material, powder bed temperature is still a determining factor that should be selected as high as possible before powder caking appears. After that, it was the laser energy density that controlled the obtained porosity, while the individual parameters such as laser powder, laser speed and scan line spacing exhibited a very slight contribution on their own. Since smoking (as a sign of degradation, reducing crystallisation enthalpy of the TPU's hard segments) intensified at higher laser energy inputs, double scanning strategies were used to minimise the laser energy density and thus the degradation in each scan. Although this approach was successful in reducing porosity (associated with a lower surface roughness) and therefore improving the mechanical properties, it failed to effectively suppress the degradation which lead to tensile properties being still much lower than those from injection moulded parts. Lastly, benchmark parts were SLSed for this TPU, showing a good geometrical accuracy but limited by the finite size of the laser spot.

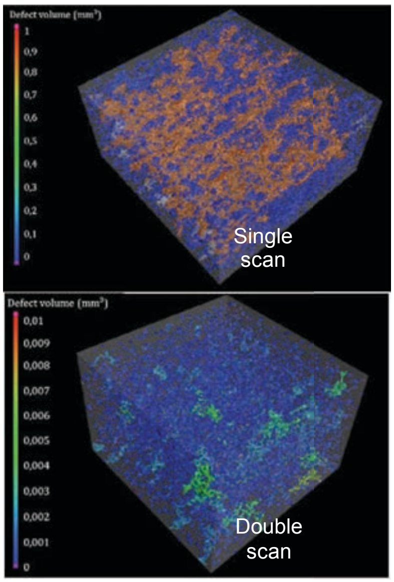

Figure 1. Reduced CT porosity via double scan

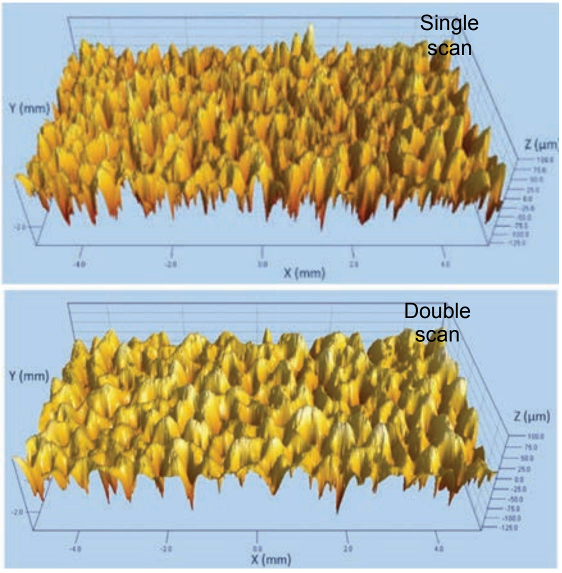

Figure 2. Reduced surface roughness via double scan

Acknowledgements: Flemish support from Strategic Initiative Materials in Flanders (SIM) and the agency for Innovation by Science and Technology (IWT) for the SIM-SBO-STREAM project PolyForce is acknowledged.

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OC21

A METHODOLOGY TO INVESTIGATE PHYSICAL AND MECHANICAL PROPERTIES OF MICRO-STRUCTURES OF A UV-CURING ACRYLATE SYSTEM

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Abstract

This work provides a method to characterize the mechanical properties of UV-cured resins used in the rapid-prototyping stereolithography (SLA) process. To that end, micrometer-sized pillars have been prepared via UV-curing (Figure 1). Subsequently, micro-compression experiments were carried out to characterize the intrinsic mechanical properties which are representative of a single UV-cured layer of an acrylate system (Figure 2a and 2b). The evolution with irradiation time of monomer conversion and glass-transition temperature has been studied first to understand at which conditions fully cured samples are obtained. Micro-compression measurements on fully cured micropillars were performed to study possible size effects[1,2] (Figure 2c). The results show a reduction in yield stress and an increase in strain hardening for decreasing pillar size. The considerations discussed can be used to understand the role of processing conditions which in the end result in specific mechanical properties studied by micro-compression and micro-tensile experiments.

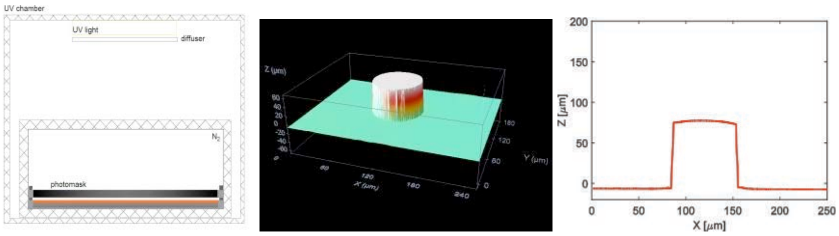
(a) (b) (c)

Figure 1 Sample preparation via stereolithography. (a) Schematic representation of UV-light chamber. (b) Example of 3D-view confocal microscope picture of pillar and (c) micropillar profile.

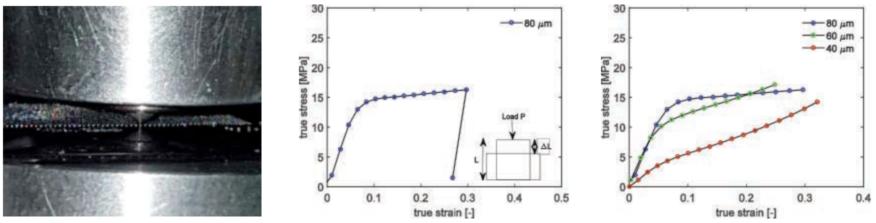
(a) (b) (c)

Figure 2 (a) Micro-compression experiments and (b) example of true stress versus true strain curve of 80µm micropillar. (c) Stress-strain response of micropillars of 80, 60 and 40 µm.

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OC22

EVALUATION OF THE FLEXURAL BEHAVIOUR OF 3D PRINTED MULTIMATERIAL BEAMS

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Abstract

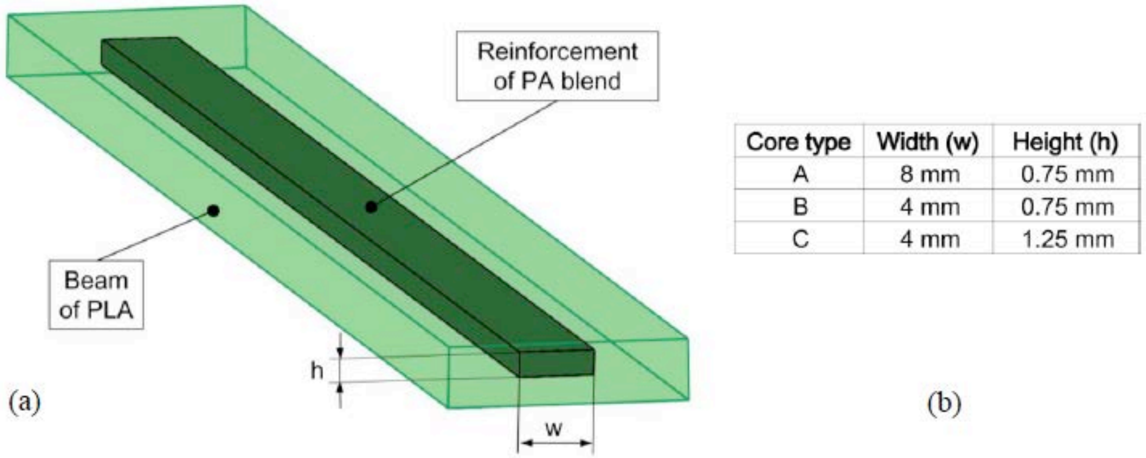
Among Additive Manufacturing (AM) processes, Fused Deposition Modelling (FDM), more popularly renown as 3D printing[1], allows the fabrication of multimaterial parts by extrusion of multiple thermoplastic filaments that are then deposited layer after layer. In such a way parts are built bottom to top and the different materials can be deployed in each cross section according to strategies aiming at optimizing the reinforcement through the exploitation of the design freedom of AM technologies.

Most diffused commercial materials for FDM are Acrylonitrile Butadiene Styrene (ABS) and the biodegradable PolyLactic Acid (PLA), that are amorphous polymers characterized by similar mechanical properties. The use of semicrystalline polymers in FDM is often avoided because of the higher amount of shrinkage which causes the warpage of the deployed layers during manufacturing. The innovative aspect of this paper is the use of a filament made of a Polyammide (PA) blend as a reinforcement in multimaterial beams of PLA that are fabricated by FDM.

The flexural behaviour of the composite beams is evaluated by three point bending tests according to the ASTM D790 method. Owing to the lack of a specific reference for 3D printing, dimensions of the specimens are assumed equal to those of injection molded specimens. Their nominal overall dimensions are 3.25 x 12.7 x 127 mm.

In this preliminary study, test specimens (Figure 1a) are 3D printed with a core of PA having a rectangular cross section, whose width (w) and height (h) are varied as shown in Figure 1b.

Bending tests show that the PA core increases both the flexural stiffness and the flexural strength of the PLA beam. Experimental results are compared with those of the finite element (FE) simulation of the bending test performed by using Abaqus/CAE software. 3D printing issues are also considered and discussed along with the influence of the layer by layer fabrication on the beam resistance.



Core type	Width (w)	Height (h)
A	8 mm	0.75 mm
B	4 mm	0.75 mm
C	4 mm	1.25 mm

Figure 1: 3D printed specimens of PLA with PA core (a); different core sizes (b).

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[1] Calignano F., Manfredi D., Ambrosio E.P., Biamino S., Lombardi M., Atzeni E., Salmi A., Minetola P., Iuliano L. and Fino P.: Overview on Additive Manufacturing Technologies. Proceedings of the IEEE 105(4), 593-612 (2017)

OC23

UNIFORMITY AND FRONTAL CONVERSION IN PHOTOPOLYMERIZATION-BASED 3D PRINTING

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Abstract

In this work, we investigate the impact of the non-uniform spatio-temporal conversion, intrinsic to photopolymerization, in the context of light-driven 3D printing of polymers.[1] The evolution of network propagation and its consequence in terms of patterned height and network conversion in photopolymerization are directly examined, considering both experiments and theory underpinning the process.[2] The polymerization kinetics of a series of model acrylate and thiol-ene systems, both neat and doped with a light-absorbing dye, is investigated. While non-monotonic conversion (Figure 1) can be detrimental to 3D printing, for instance in causing differential shrinkage of inhomogeneity in material properties, we identify opportunities for facile fabrication of modulated materials in the z-direction (i.e. along the illuminated axis). Our simple framework and model, based on directly measured parameters, can thus be employed in photopolymerization-based 3D printing, both in process optimization and in the precise design of complex, internally stratified materials by coupling the z-stage displacement and frontal polymerization kinetics.

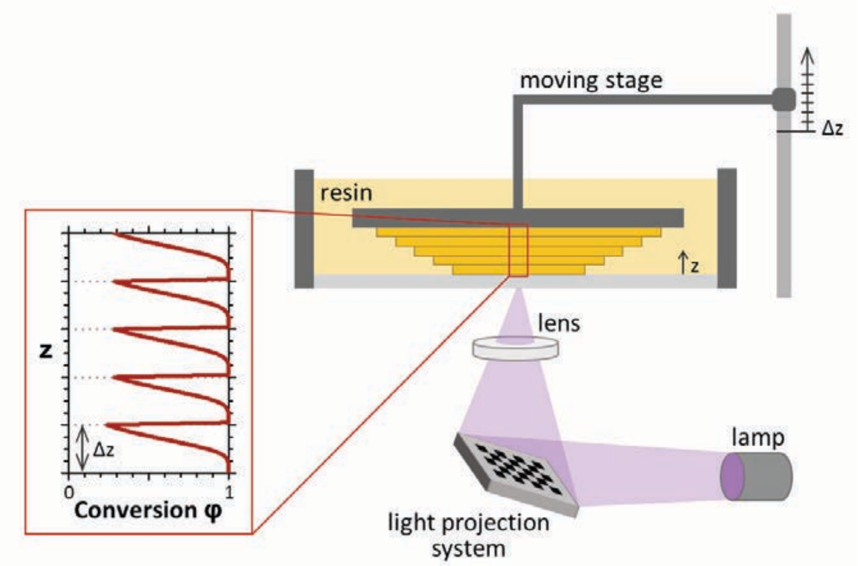

Figure 1. Non uniformity in 3D printing based on photopolymerization: each processed layer, with a thickness equal to Δz, is characterized by a non-constant monomer-to-polymer conversion φ, which shows a sigmoidal profile.

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[2] A. Vitale, M. G. Hennessy, O. K. Matar, and J. T. Cabral, *Advanced. Material.* **27**, 6118 (**2015**).

OC24

INFLUENCE OF PROCESSING CONDITIONS ON THE TEMPERATURE FIELD AND ON THE MECHANICAL PROPERTIES IN FDM

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Abstract

FDM has been used for long in industry for prototyping but has moved into production of functional parts thanks to progress in the reliability, repeatability and precision of the machines. However, some improvements still have to be made with materials, conception and process control to enhance the mechanical properties of the parts and guarantee their integrity during service.

The key factor in filaments bonding is the thermal energy of the extruded polymer and the driving mechanisms are the coalescence (formation and growth of a neck between adjacent filaments) and the molecular diffusion and randomization of the polymer chains across the interface. Therefore, the temperature history of the interface is crucial in determining the quality of bonding and thus the mechanical properties of the final product.

This presentation illustrates some experimental work and numerical simulations using a full transient Finite Elements Model aimed at analyzing the influence of process conditions on the mechanical properties of FDM parts. Especially, the computations of the temperature profile in filaments deposited on top of one another (Figure 1) allow to understand better the influence of processing conditions (nozzle temperature, layer height and fiber width set by the software).

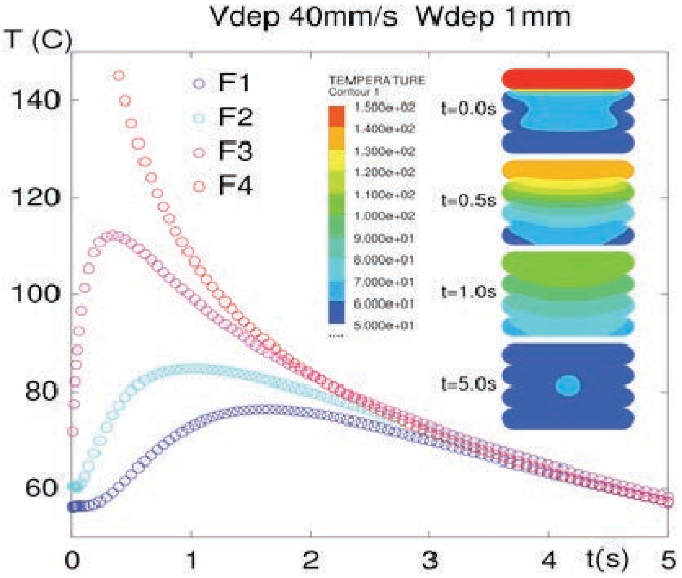

Figure 1: FEM computations of the temperature of four filaments deposited in FDM (from F1 to F4).
Open symbols: plots of the average filament temperature vs. time for ABS material, deposition velocity 40 mm/s, deposition width 1mm.
Inset: contours of the temperature field at t = 0 s, 0.5 s, 1 s, 5 s.

OC25

OPTIMISTION OF SELECTIVE LASER SINTERING PROCESS

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Abstract

Thermoplastic parts obtained by selective laser sintering of a powder bed (SLS process) have porosities which significantly reduce their mechanical resistance[1,2]. These porosities are due to trapped air between polymer grains while polymer melts and grains coalesce. To understand the physical mechanism involved in the powder densification, the anisothermal coalescence of a powder bed has been simulated after the passage of the laser beam.

Firstly we show that coalescence of spheres leads to roughly the same coalescence time as cylinders. It allowed us performing a 2D simulation using a C-NEM method implemented in Matlab® to assess the importance of the different physical phenomena involved in the process: polymer powder grain coalescence, interface welding, process temperatures, powder laser energy absorption. Two polymers were considered in the simulations: a PEEK and a PEKK. Surface tension and viscosity of studied polymers, which pilot coalescence phenomenon, were measured versus temperature. The geometry of powder bed was determined by Xray tomography. Laser absorption of thermoplastic powders were identified though a specific device and a calorimeter. The simulation was validated by comparing the simulation of flows for of known simple geometries: cylinder coalescence and pendant drop. The simulation was calibrated by adjusting thermal exchange coefficients thanks to measured melted depth.

We have determined thermal and time orders of magnitude of the process. We mainly show that the temperature of the polymer may rise by several hundred degrees [3] and decreases in a few tenths of a second, while densification process can take several tens of seconds. We have determined the processing window for semicrystalline polymers. Then we could conclude that only amorphous thermoplastic powder with a very low molecular weight can be processed by SLM process.

Acknowledgments:
The work was done in the framework of the French FUI project FADIPLAST coordinated by Dr Gilles Surdon (Dassault Aviation)

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[2] Dupin et al., *European Polymer Journal*, 2012.
[3] Peyre et al., *Journal of Materials Processing Technology*, 2015

OC26

INFLUENCE OF FDM PROCESS PARAMETERS ON PLA/OMMT NANOCOMPOSITES: A RHEOLOGICAL AND MECHANICAL APPROACH

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Abstract

Additive manufacturing techniques employ more and more polymers. However, charged polymers are under studied – compared to other shaping processes – while they are a way in the small serial production of end-use products with specific properties and geometries. With the Fused Deposition Modeling technique, clogging nozzle is a persistent hinder to the use of micrometric fillers due to their size. On the contrary, nanometric ones have smaller dimensions and develop a high specific surface area which allows a modification of mechanical properties with a lower amount (usually 1-10 %wt instead of 20-60 %wt).

To understand the relation between rheological behaviour of nanocomposites and their capability for shaping in FDM, this research studied nanocomposites based poly(acid lactid) and charged with organo-modified montmorillonite at 0, 0.5, 1, 3 and 5 %wt. On the one hand, nanocomposites were characterized by oscillatory and capillary rheology. On the other hand, designs of experiments were conducted to analyse the impact of different FDM parameters such as manufacturing speed, temperature, layer thickness and deposition angle on tensile properties (Fig. 1). Mathematical models have been formulated by Taguchi method and then by Doehlert one to (i) know which factors have an effect and (ii) visualize how parameter value changes tensile properties.

Adding fillers modified the materials properties, thus the higher the amount of fillers was, the better the printability was observed. The results showed (i) a decrease of factor effects on Young's modulus and ultimate strength when fillers are adding and (ii) a non-linear variation on the same properties with manufacturing speed and temperature (Fig. 2). The determined optimum setting and the viscosity at high shear rate also varied between the different formulations with a discontinue evolution before and after around 1 %wt. These findings have significant implications on the mechanical optimization and the understanding of FDM process parameters with respect to the rheological properties of nanocomposites.

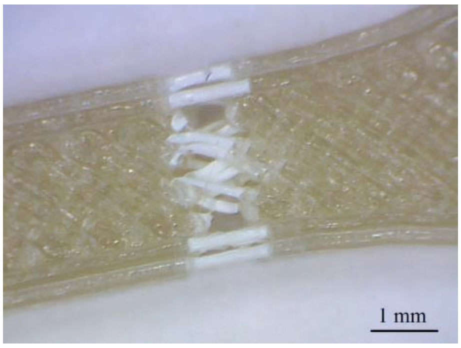

Fig. 1 Rupture of a nanocomposite tensile test specimen fabricated by FDM with a deposition angle at +45°/-45°

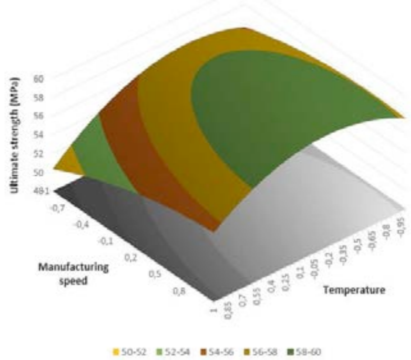

Fig. 2 Modeling of ultimate strength of a PLA/MMT nanocomposite as a function of manufacturing speed and temperature (coded units)

OC27

CONTROLLING POLYMER MORPHOLOGY IN ADDITIVE MANUFACTURING

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Abstract

Additive manufacturing is an emerging family of processes which enable products to be produced from a digital definition without the use of specific tooling or moulds. It facilitates mass customisation and as a consequence it is particularly suited to applications in the medical field where the objects can be personalised to the patient. Although additive manufacturing has evolved far from the domain of prototyping, little attention has been directed at the impact of the manufacturing technology on the morphology and structure of the polymeric material in the final part. The morphology and structure of the polymer is an important component in determining the properties of the part as in any polymer processing technology[1]. In this work we focus on the impact of 3d printing processes on the morphology of polymers, especially crystallisable polymers. We use x-ray scattering techniques to evaluate the polymer morphology on multiple length scales. We find that in the case of poly(ε-caprolactone), the most significant operational parameters to influence the morphology are the deposition speed, the extrusion speed and the extrusion temperature. In essence, the extrusion process can lead to a deformation of the molecular chains in the melt and if that deformation has not relaxed by the time crystallisation begins then the crystallisation is directed by that deformation. Equally we can add components to the poly(ε-caprolactone) to modify this behaviour such as nucleating agents either in the form of graphene nanosheets or self-assembling fibrils formed from low molar mass compounds.

To demonstrate the opportunities which morphological control during additive manufacturing provides we have prepared some solid cubes which have a gradient in morphology written in to the cube.

Controlling or defining the morphology has a major impact on properties. We show that we can define the morphology and hence properties by using the operational parameters, rather than by varying the composition or adjusting the dimensions of the product. This control will impact on many properties including degradation rates in the case of biodegradation rates of medical implants as well as mechanical properties.

This work was performed as part of the UC4EP (Understanding Crystallisation for Enhanced Polymer Properties) at CDRSP P2020-PTDC/CTM-POL/7133/2014 Funded by FCT and also through the Strategic Project UI 4044. The x-ray scattering measurements were performed in the Chemical Analysis Facility at the University of Reading and at the Non-Crystalline Diffraction Beamline at the ALBA Synchrotron with the collaboration of ALBA staff.

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[1] "Controlling the morpgology of polymers: Mutiple scales of structure and processing", Editors Geoffrey R Mitchell and Ana Tojeira 2016 Springer Switzerland

POSTER CONTRIBUTIONS

P1

ANALYSIS OF LOW MOLECULAR WEIGHT POLYMERS USING LATEST ADVANCED MULTI-DETECTOR GPC SYSTEMS

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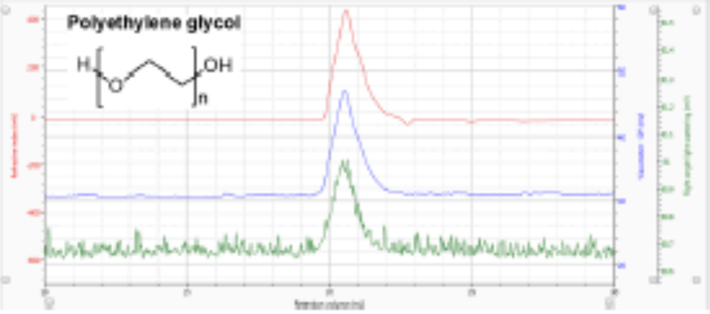
Abstract

Gel-permeation chromatography (GPC) is the most widely used tool for the measurement of molecular weight and molecular weight distribution of natural and synthetic polymers. Advanced detectors such as light scattering are increasingly used to overcome the limitations of conventional GPC measurements and offer *absolute* molecular weight. A viscometer measures intrinsic viscosity, a key structure factor that can be used to calculate branching levels and can be combined with molecular weight data to calculate hydrodynamic radius. In combination these data allow detailed structural information of a polymer to be generated in a single GPC measurement which can be compared with other samples in Mark-Houwink plots. This can be used to study substitution or branching levels.

Among the practical challenges when making light scattering measurements is sensitivity to the light scattered by the sample. Sensitivity is limited by a polymer's molecular weight, concentration and dn/dc. In the development of novel polymers, limitations in any of these areas are common. For instance, drug delivery polymers such as PLGA often have low dn/dc, while coating polymers such as epoxies and smaller components such as polyols can have extremely low molecular weight. Of course, many polymers, particularly during their early development are only available in limited quantities, which restricts the amount of material that can be loaded on to the column. The high sensitivity of the light scattering and RI detectors extend the lower sensitivity limit for polymer measurements and we can now measure polymers that before were not detected by GPC detectors.

In this paper, we will discuss how the class leading sensitivity of Malvern's latest GPC system, OMNISEC, can be used to overcome these challenges. Using examples of epoxies, polyols, and PLGA, we will show how advanced detection can now comfortably be used in these difficult application areas widening its overall utility.



Multi-detector SEC chromatogram (RI, RALS and Viscometer detectors) of Polyethylene Glycol with Mw of 196 g·mol^{-1}. Sample concentration used 3.9 mg/ml.

P2

THERMAL AGING AND PROPERTIES OF POLYMERIC MATERIALS FOR SELECTIVE LASER SINTERING

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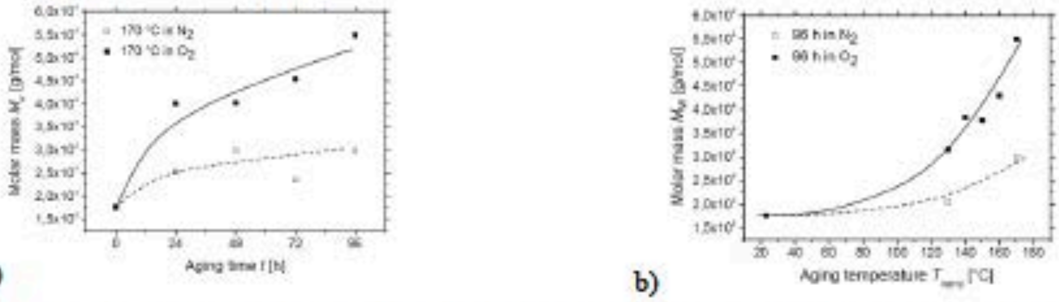
Abstract

During selective laser sintering (SLS) the polymer is exposed to elevated temperatures for extended periods of time. Although the thermal aging of polymers in the solid state is much slower than in the polymer melt, and the thermo-oxidative degradation is suppressed by the nitrogen atmosphere, the retention times during SLS are considerably longer than typical for classical polymer melt processing such as extrusion or mold injection.

Structure and property changes of polyamide 12 powders for selective laser sintering and of sintered test specimens were investigated after different thermal aging times under nitrogen and in air by differential scanning calorimetry, dynamic-mechanical analysis, light microscopy, impact tests, melt rheology, gel permeation chromatography, infrared spectroscopy and thermogravimetric analysis.

Powders and sintered test specimens were isothermally aged in air and in nitrogen at discrete temperatures between 130 and 170 °C and removed after defined aging times (24, 48, 72 and 96 hours) for the measurements. For comparison fresh powder and unaged test specimens were included. It was found that the average molar mass of the powders increases with increasing aging time (Fig. 1a) and aging temperature (Fig 1b).



a) b)

Figure 1: Average molar mass M_w of polyamide 12 as a function of aging time (a) at 170°C and aging temperature (b) under nitrogen (open symbols) and in air (solid symbols).

Fig. 2 shows the frequency dependence of real (*G*') and imaginary part (*G*'') of the dynamic shear modulus *G** of PA12 after different isothermal aging times in the melt at 190 °C. The changes in the frequency dependence indicate the increase of molar mass or the formation of cross-links.

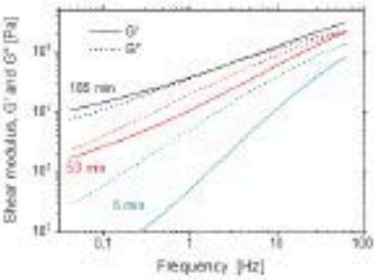


Figure 2: Frequency dependence of *G*' and *G*'' of polyamide 12 after isothermal aging times of 5, 53 and 185 minutes at 190 °C in the melt.

For melt rheological measurements of thermally aged powders test specimens (parallel plate geometry) were prepared by hot pressing under vacuum. For longer aging times at higher temperatures chain degradation is detectable in the rheological spectra. For the aging mechanism therefore interplay between chain extension/cross-linking and thermo-oxidative degradation is assumed.

P3

3D PRINTING FILAMENTS: CHARACTERIZATION OF A NEW CLASS OF COMPOSITE MATERIALS

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Abstract

3D modeling and printing techniques are spreading in daily life as solutions or implementations of objects production. Among the advantages that these technologies have brought in industrial and niche sectors, the possibility to create specific solid models from a digital design is at the base of the popular employment in prototyping[1],[2]. Moreover, there are fields such as biomedical devices and cultural heritage conservation, where the printing of unique objects is a peculiarity. For example, reconstructing fragmented artworks is a complex and time-consuming process and the use of low-cost techniques of 3D printing for the restoration of missing parts can be a strong improvement. However, long-term-durability at environmental conditions, compatibility with the artefact and reversibility are significant, yet often neglected, issues[3].

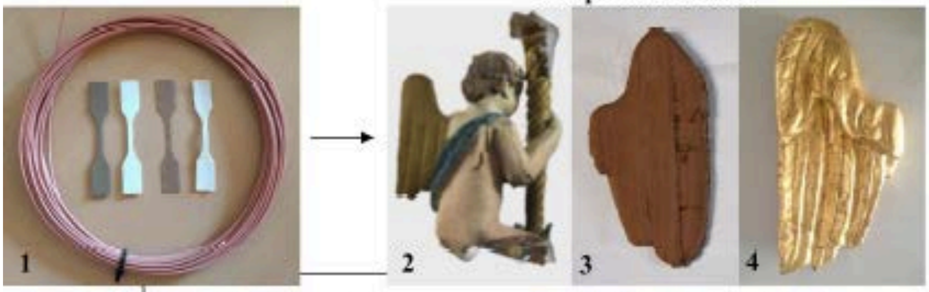
Fused deposition modeling (FDM) is an additive manufacturing technology that builds up parts layer-by-layer, by heating and extruding suitable filaments[4]. Filaments are based on thermoplastic polymers, sometimes enhanced with fillers, in order to obtain particular colours or materials effects (e.g. being similar to wood or metal), more than improved mechanical properties. Even though they are composite materials and this may have an effect on their workability and lifetime, this aspect is not often taken into consideration by producers and artisans.

In the present study, several filaments have been characterized to evaluate the influence of filler addition and changes eventually induced during the printing step, from chemical modifications to VOCs release. In particular, FTIR-ATR, TGA, DSC, Py- and SPME-GC/MS together with mechanical tests have been carried out on original, printed and aged materials. The results have then been considered in light of the often limited specifications supplied by the producers, i.e. printing suggestions and material performances, that are often given without considering work-conditions, neither indicating if suitable for external environment.

The clue of a limited characterization of the commercial materials has risen by observing how some filaments are heated up to temperature higher than their offset temperature of degradation. In other cases, a chemical modification has been detected just leaving the unprinted material in a drawer in laboratory environment conditions.

This work aims to introducing the most peculiar results of this research, underlining potential materials weaknesses.

Graphical abstract



1: filament for FDM printing technique and specimens for mechanical characterization.
2: wooden sculpture, cherub with a missing wing
3-4: printed wing to be placed on the sculpture before and after finishing

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[4] Turner B.N., Gold S.A.. Rapid prototyping journal, 21/3 (2015) 250-261

P4

RAPID PROTOTYPING BY ADDITIVE MANUFACTURING OF EQUIPMENT FOR WINTER SPORTS

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Abstract

Thermoplastic polymers are widely used for the production, by injection moulding, of winter sport equipment, such as for example ski boots. The highest cost in the development of a ski boot is the preparation of the moulds for the external shell that can cost, for a single size, up to 50000 euro. Any modification of the moulds during the development process adds additional costs. Moreover, the time needed to produce a mould can require up to 4 weeks, which significantly retards the development process. For this reason, in the last few years, ski boot producers are looking for rapid prototyping techniques in order to decrease the development process time and costs. However, materials for ski boots (and plastic materials for winter sports equipments in general) must complain to several thermo-mechanical characteristics. In particular, they must resists to impacts at temperatures as low as -20°C and must provide the correct flexural and damping characteristics to obtain the optimal skiing performances. However, the materials actually used for 3D printing lacks of some or all of the characteristics necessary to produce a ski boot prototype. Therefore, the aim of this project has been the comparison of the techniques and of the materials actually present on the market for 3D printing rapid prototyping in order to determine the modification in terms of materials and printing technique necessary to obtain prototypes with thermo-mechanical and safety characteristics that permit their use in on-snow tests.

We have prepared specimens for tests and ski boot shells using Selective Laser Sintering (SLS) and Fuse Deposition Modelling (FDM) techniques. The test specimens have been prepared using 3 orthogonal orientation of growth in order to determine the anisotropy of the materials printed. Two sets of materials have been tested for both 3D printing techniques; the 3D printed materials have been characterized using DMTA analysis to measure their stiffness and damping behaviour and by Izod impact tests at 23°C and -20°C in order to assess their impact resistance. Ski boot shells and other parts of the ski boots have then been prepared and analysed in the test benches used to measure the flexural stiffness and the rebound speed of ski boots, comparing their properties with those of commercial ski boots.

The results obtained indicate that it is possible to obtain ski boots prototypes by 3D printing that can be safely skied using Nylon 12 composites with carbon or glass fibers. However, new materials must be developed in order to obtain the same performances of a ski boot prepared using the injection moulding process.

P5

STRAIN MONITORING OF CARBON NANOTUBES NANOCOMPOSITES BY FUSED DEPOSITION MODELLING

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Abstract

Development of novel nanocomposites for fused deposition modelling (FDM), one of the most widely diffused additive manufacture technology, offers a challenge for enhancing the properties of 3D-printed components[123]. In present work, the strain monitoring possibilities offered by carbon nanotubes (CNT)/acrylonitrile-butadiene-styrene (ABS) nanocomposites for FDM were investigated. Various concentration (1 to 8 wt%) of CNT were melt dispersed in ABS by melt compounding, followed by extrusion to produce filaments. ABS filled 6wt% of CNT were selected and investigated for the FDM process at different infill pattern: horizontal concentric (HC) and horizontal infill 45° (H45).

The presence of carbon nanotubes in host ABS matrix induced a remarkable enhancement in mechanical and electrical properties on both filaments and 3D-printed components. Conductive 3D-printed samples HC and H45 were subjected various mechanical loading conditions (tensile and cyclic load) and electrical resistance was monitored simultaneously. The electrical resistance simultaneously changed in **Figure 1** with calculated gauge factor of 2.7 and 6.5 for HC and H45 respectively. The creep behaviour with simultaneous resistivity response will be discussed, and the effect of temperature will be also considered.

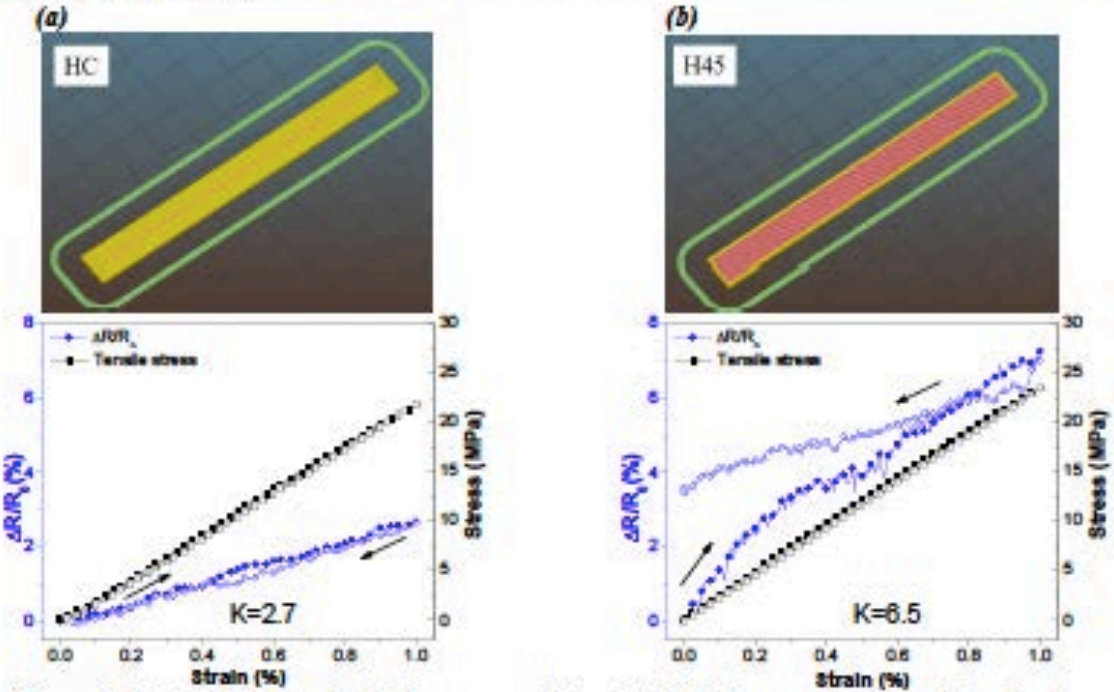

Figure 1. Electrical and mechanical response of 3D-printed CNT6 nanocomposites during loading (full symbol) and unloading (open symbol) under tensile test: (a) HC and (b) H45 directions.

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[2] S. Dul, L. Fambri, and A. Pegoretti, *Composites Part A, Applied Science and Manufacturing*, **2016**, *85*, 181.
[3] A. Dorigato, V. Moretti, S. Dul, S.H. Unterberger, and A. Pegoretti, *Synthetic Metals*, **2017**, *226*, 7.

P6

RHEOLOGICAL PROPERTIES OF FRESH CONCRETE – MOLECULAR ORIGIN ANALYZED BY NOVEL COMBINED RHEOLOGICAL METHODS

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Abstract

Concrete is, after water, the most widely used material on the planet. In 2017, the world population is estimated to be 7.4 billion people meaning that there is an average of about 4000 Kg of concrete per person per year. Durability and serviceability play a key role in designing a sustainable process for humanity, and this can be accomplished by extending the service life of concrete structures. The increased need for more detailed experimental data and a better understanding of the relevant molecular mechanisms involved in concrete flow and deformation has led to the search for new experimental techniques for the characterization of transient structural changes during mechanical processes. We have developed several globally unique combinations where rheology and spectroscopic methods are combined to investigate the macroscopic mechanical properties from a molecular point of view. Portland cement: CEM I 42.5 R was analyzed by multiple combined techniques including Rheo-Dielectric[1] (Fig.1), Rheo-NMR[2,3] (Fig.2), Rheo-SAXS and FTIR.

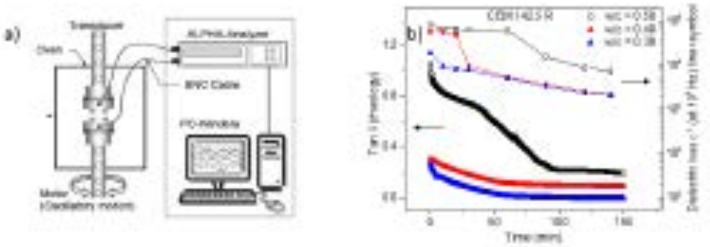

Fig.1 Simultaneous Rheo-dielectric measurements performed to characterize the time evolution of the rheological and dielectric properties of fresh concrete. a) Experimental setup b) Correlation between tan δ and the dielectric loss at 10^5 Hz in the dielectric medium.

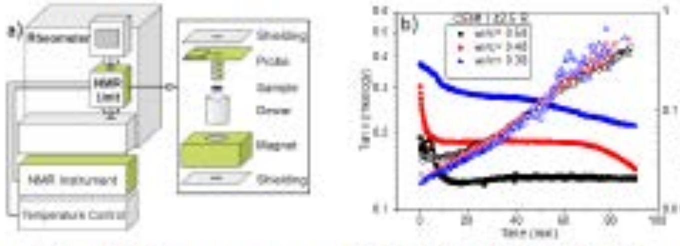

Fig. 2 Simultaneous Rheo-NMR measurements. a) 30 MHz NMR Halbach magnet with magnetic shielding set in an ARES rheometer b) Simultaneously measured rheological tan δ (full symbols) and NMR parameter T_2 (open symbols) as a function of time.

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[2] T. Meins, K. Hyun, K. Ratzsch, C. Friedrich, B. Struth, M. Wilhelm; (2011), *Combined methods in Rheology: Rheo-SAXS, Rheo-NMR and Rheo-Dielectric to bridge length and time scales*, Annual Transactions the Nordic Rheology Society, 19, 201

[3] J. Rottstegge, M. Wilhelm, H.W. Spiess; (2006), *Solid state NMR investigations on the role of organic admixtures on the hydration of cement pastes*, Cement & Concrete Composites, 28, 417-426

P7

POLYMER MATERIALS FOR 3D PRINTING OF MICROREACTORS

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Abstract

Additive manufacturing (AM), also referred to as 3D printing technology, is a term for all technologies that build 3D objects by adding layer-upon-layer of material. Additive manufacturing is being used to fabricate molds, prototypes and functional parts with complicated geometry. Depending on the technology, materials used for the production of an object can be in powder, liquid or solid form. The most commonly used are polymeric materials (ABS – acrylonitrile/butadiene/styrene, PLA – polylactide, PET – poly(ethylene terephthalate), etc.), but also, less frequently metals and their alloys, ceramics and composite materials are used.

Microreactors are reaction systems fabricated in microscopic scale by using, at least partially, methods of microtechnology and precision engineering.[1] The selection of materials for microreactor manufacturing greatly depends on the desired application and on several of the parameters: the type of reaction that is carried out, chemical compatibility with solvents and reagents, the type of microreactor, the mechanical requirements of the microreactor, price, availability on the market, ease of production, etc.

The aim of this work was to investigate commercial polymeric materials in order to replace glass materials in microreactor production. In this paper the effects of solvents (water, ethanol and acetone) on materials used in the fused deposition modeling (FDM) additive manufacturing technique were investigated. Effect of solvent was tested by using swelling tests to see which material is suitable for microreactor production. Materials were characterized by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC), and also, mechanical properties of all the materials were tested.

This work has been supported by Croatian Science Foundation under the project entitled "Development of materials for 3D printing of microreactors" (UIP-2014-09-3154).

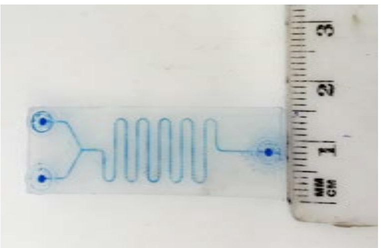

Figure 1. 3D printed microreactor

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P8

VISCOSITY CONTROL OF NYLON 66 THROUGH AMIDE-BASED OLIGOMERS FOR HIGH-LOADING GLASS FIBER COMPOSITES

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Abstract

Aliphatic polyamides (nylons) are representative engineering plastics with versatile applicability, good mechanical strength, and thermostability. Melt viscosity control of these polyamides is an important issue concerning polymer processing and additive selection. The quality and productivity of composites are directly influenced by the melt viscosity in extrusion and injection molding processes, since short cycle times and accessibility to the fine structure of the molder depend on it. The melt viscosity is especially important in composites with >40% fiber in which fast and complete impregnation into the fine spaces between fibers is needed.In this study, application of amide oligomers to effectively control the melt viscosity of polyamides was proposed. In order to investigate the structural effects of these oligomers on nylon resins and the influence of their constitutional form, cyclic and linear oligomers were selectively prepared from nylon6 and nylon66 by depolymerization and transamidation. When applied to the nylon66 resin, linear oligomers provided a greater melt viscosity-lowering effect than that in the cyclic oligomers. The effect of the repeat unit structure was investigated by preparing and applying oligomers based on nylon66, nylon6, and nylon46. The nylon6-based oligomer with sufficient hydrogen bonding interactions, but also inducing hydrogen bond mismatching in the polymer network showed the greatest viscosity-lowering effect, while the 66-based oligomer with perfect hydrogen bond matching with matrix nylon66 had a reduced viscosity-lowering effect. Addition of the nylon6-based linear amide oligomer into 40% glass fiber composites of nylon66 increased the melt flow index more than 2 times with little effect on mechanical properties. Thus, it is worth considering combination of amide oligomers with aliphatic polyamides as an additive to control the viscosity.

Acknowledgment.

This work was supported by the Technology Industrial Innovation funded by the Ministry of Trade, Industry & Energy(MI, Korea) [grant number 10050523]

P9

THE CRITICAL PROPERTIES TO CONTROL THE QUALITY OF PAEK PARTS IN ADDITIVE MANUFACTURING

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Abstract

The processes for additive manufacturing (AM) of polymers mainly include filament deposition, selective laser sintering (SLS) and stereolithography. However, the polymers used in these technologies are limited to low heat resistance polymers with low stiffness, whereas aerospace and high-tech industries require high performance polymers, that it means, thermal resistance higher than 200 °C in continuous using, elastic modulus higher than a few GPa and low sensitivity to thermo-oxidative ageing. The polymers of PAEK (polyaryletherketone) family are the most durable among high performance thermoplastics: they keep their mechanical properties for a longer time when exposed to temperature close to their glass transition[1]. Among them, PEEK (polyetheretherketone) has been used for 35 years. Despite its potential, manufacturing PEEK parts by 3D printing remains a challenge. Oppositely, polyamide is suitable for SLS, because of its wide processing window, narrow melting temperature and low melt viscosity[2]. The properties of PEEK do not stimulate to additive manufacturing. Nevertheless, some works aim to predict the mechanical properties of PAEK parts manufactured by SLS process[3]. Pointing out the critical properties of PAEK polymers for AM processes would open the possibility to spread them in additive manufacturing, which could be a step forward for the European industrial innovation.

Previous studies show that the interlayer adhesion is driven by the viscosity and the surface tension of polymers. This work focuses on the properties of PAEK playing a role in the coalescence phenomenon: rheometric properties, thermal properties and surface tension. Firstly, thorough knowledge of thermal transitions is essential to control the interfacial adhesion and the degree of crystallinity of manufactured parts. The influence of cooling rate on the degree of crystallinity was studied. It is clear that the cooling of PEEK parts during manufacturing must be controlled in order to promote crystallization. However, before cooling of the last deposited layer, the macromolecules must have enough time to interdiffuse from the latter layer to the previous one. Dynamic rheometry tests using parallel plates configuration were carried out at different isothermal temperatures. For the low shear rates involved, the viscosity at the Newtonien plateau is close to 10000 Pa.s, it means that the diffusion time of the macromolecules at the interfaces takes a few seconds, what does not foster the interlayer adhesion. The viscosity increases drastically for the highest temperatures due to chain breakage followed by recombination which result in rising viscosity[4]. The next step of this work will be to change these properties to promote the interlayer adhesion in order to master the mechanical properties of PEEK parts manufactured by laser sintering and filament deposition.

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P10

PREVIEW: predictive system to recommend injection mould setup in wireless sensor networks

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Abstract

In the last years, a constant demand of diversity and personalisation in the plastic sector industry has led to a change of the manufacturing paradigm. Current globalisation models, often force production forecasts to adapt to tight and ever-changing schedules, resulting in injection moulds being rotated from one machine to the other, or even in between international production sites. Moreover, short productions demand a high degree of flexibility, leading to an increased number of mould changes in plastic moulding factories, causing downtimes and scraps. A reduction of the mould setup time for each machine and a reduction of the reject rates are highly demanded within this context.

PREVIEW addresses both goals by recommending the optimum machine parameters of the injection process through monitoring and analysing real time and historical data. A cyber physical system was developed for plastic injection manufacturing processes monitoring, control and optimisation by incorporating several innovative and cutting edge technological solutions: advanced artificial intelligence and machine learning techniques, robust industrial wireless communication, Internet of Things (IoT) and wireless indoor localisation. In the PREVIEW system, real time data are acquired from both mould cavity sensors and the machine programmable logic controller, wireless transmitted to the centralised server, modelled and analysed by means of machine learning algorithms. Finally via an indoor location system, machine performances and recommended optimum parameters are displayed on the operator's tablet/smartphone (figure 1). PREVIEW aims at reducing mould set up time, reducing scrap and energy consumption and increasing the flexibility and productivity[1].

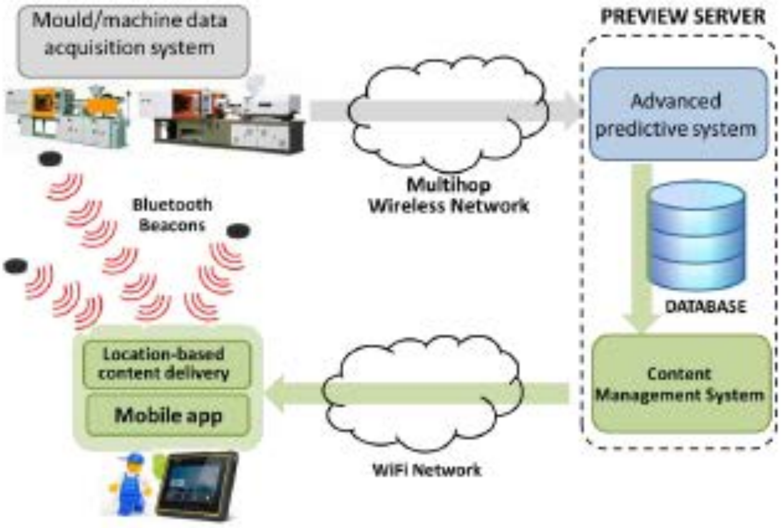

Figure 1. PREVIEW system approach

Acknowledgements

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[1] www.preview-project.eu

P11

Sensorised moulding: combining precision with sustainability

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Abstract

The need for more efficient, self-sufficient manufacturing processes drives current industrial settings, forecasts, regulations and revenues. The imposition of higher pollution taxes and emission limits are forcing industrial polymer manufacturers to find alternative routes for process optimisation and sustainability. The injection moulded plastic market size was calculated to be at over 100 million tons in 2015, with a growth forecast of more than 5% compound annual growth rate (CAGR) by 2023[1]. This supposes a major contribution to energy consumption and emission values. Due to its significant volume, even minor savings at each step of the injection moulding process can lead to significant savings. In this study, we extrapolate the use of pressure and temperature sensors fitted in the injection mould cavity of an Arburg All-rounder 420C 1000-350 (1996 model) to calculate real-time process specific energy consumption (SEC) values that can help to identify any process inconsistencies and determine its environmental footprint for tools such as life cycle assessments (LCA).

The analysis uses the combined methodologies of Thiriez[2] and Madan[3], to define a single SEC value through the equation: $SEC=E/m$, where E stands for energy and m defines the shot size. The pressure and temperature parameters (p_{inj}, T_{inj}, T_{ej}) input into the calculations were obtained from mould cavity sensors data (Figure 1a). The predictions were verified against energy measurements using an energy logger, showing an accuracy of between 70-60% (Figure 1b). The ability to extract this data from any mould, particularly those used in machines without an appropriate graphic interface presents significant benefits in process monitoring and environmental control to the large active sector of injection machines produced during the 1980s and 1990s that are still in use. The study concludes with a brief LCA analysis of the energy and material savings that can be made when using cavity sensors data for process monitoring.

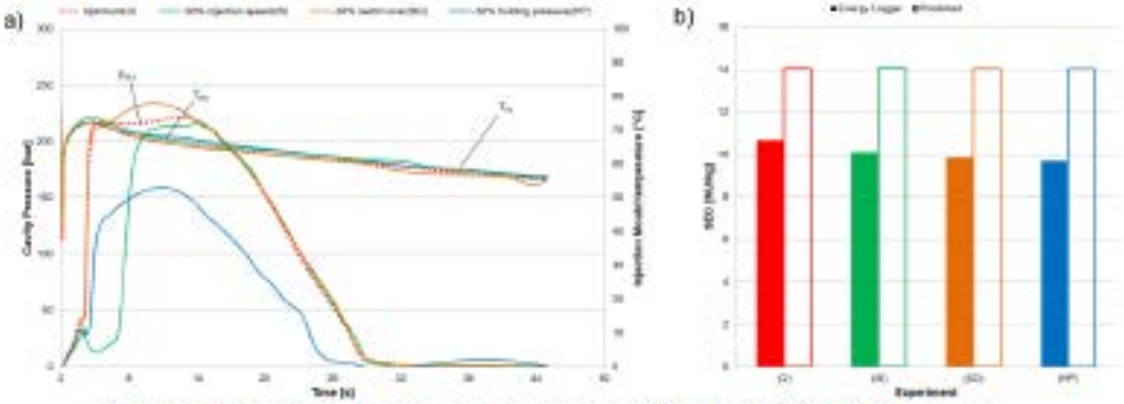

Figure 1. a) Cavity sensors process data along with b) its corresponding SEC calculations.

Acknowledgements

This research forms part of the PREVIEW project, kindly funded by the European Union's Horizon 2020 Research and Innovation Programme, grant agreement no. 636892.

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P12

A STUDY OF THE EFFECT OF PROCESS PARAMETERS ON THE PERFORMANCE OF A 3D PRINTED POLYLACTIC ACID

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Abstract

A Design of Experiments was applied to evaluate the influence of some process variables and, if any, of their interaction on the mechanical behaviour of specimens built up with a Fused Deposition Modelling (FDM) process. The study is a preliminary step of a work, which is aimed at defining guidelines for a proper design of a product in relation to its mechanical requirements.

The material used in this work is a poly(lactic) acid and the process variables considered are: the operating speed and temperature, the layer height, the raster orientation and the number of perimeters. Combining differently the processing variables, 32 different specimens were produced. A tensile test was performed on each specimen and the apparent tensile strength was measured. A two-level fractional factorial design with resolution V was adopted.

As far as the main factors, as expected a monotonic dependence of the tensile strength on the raster orientation and on the number of perimeters was observed, while a non-monotonic trend was observed as far as the effect of both the number of layers and the applied speed.

By the surface plots analysis, it seems there is some effect of parameters interaction on the mechanical response of the 3D printed specimen, but further work is still required for a better interpretation of the obtained results.

P13

NEW POLYMERS FOR ADDITIVE MANUFACTURING: POLYETHERS, POLYACRYLAMIDES AND POLYESTERS

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Abstract

As additive manufacturing gains popularity, more polymeric materials must be developed to satisfy specialized needs in the field. Although not of the lowest cost, polymers of well-defined structure and known molecular weight and composition represent model systems whose evaluation in additive manufacturing would provide accurate structure-performance relationships and help design better materials. This work will present the preparation and characterization of three such classes of polymers which can be evaluated in additive manufacturing, two of which can be printed from aqueous solution, and the third from the melt. The first class comprises water-soluble, four-armed star poly(ethylene glycol)s (tetraPEG stars), a part of which is end-functionalized with aldehyde and another part with the chemically complementary acylhydrazide; mixing of aqueous solutions of the two leads to the formation of hydrazone bonds and consequent gelation[1]. The second class consists of two types of linear water-soluble polyacrylamides, one also bearing aldehyde groups and the other also bearing hydroxylamine groups; mixing of aqueous solutions of the two results in the formation of alkoxime bonds and consequent gelation. The third class involves semicrystalline polyesters of a diacid, sebacic acid (1,8-octanedicarboxylic acid),[2] which can be printed from the melt. The preparation, functionalization, and characterization of the molecular weights and composition of all the polymers will be reported, and preliminary printing results will be presented.

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P14

MEGALIN-TARGETED ENHANCED TRANSFECTION EFFICIENCY IN CULTURED HUMAN HK-2 RENAL TUBULAR PROXIMAL CELLS USING AMINOGLYCOSIDE-CARBOXYALKYL-POLYETHYLENIMINE-CONTAINING NANOPLEXES

MOHAMMAD RAMEZANI[1], FATEMEH OROOJALIAN[2], ALI HOSSEIN REZAYAN[2], WAYNE THOMAS SHIER[3], KHALIL ABNOUS[1]

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Abstract

WITHDRAWN

P15

PHOTO-CATALYTIC POLYMERIC ADDITIVES FOR PLA

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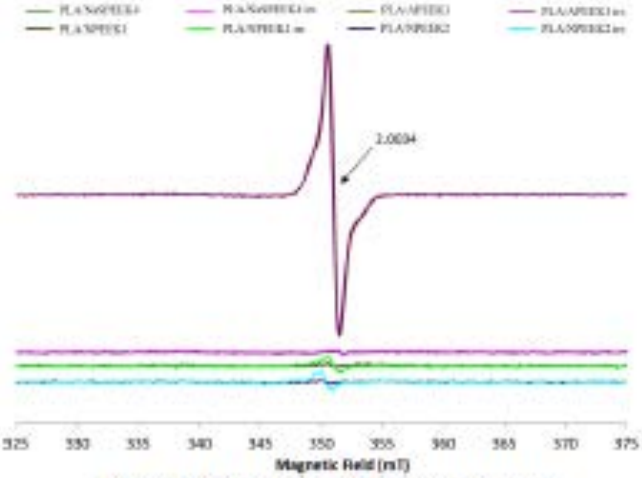
Abstract

Polylactic acid (PLA) is an attractive candidate for replacing petrochemical polymers as it is obtained from renewable resources. Inclusion of additives into PLA can extend the range of potential applications of this material, including those in which self-cleaning properties and the ability to degrade organic pollutants or contaminating micro-organisms is desirable. The latter properties could be promoted by incorporating photocatalytic additives allowing to switch on the desired behaviour upon exposure to suitable UV radiation[1]. In this study, three polyether-ether-ketone (PEEK) derivatives have been synthetized as photocatalytic additives: PEEK sulfonate (SPEEK), PEEK nitrate (NPEEK) and amino-PEEK (APEEK). The various PEEK derivatives were successfully obtained with a controllable functionalization degree as confirmed by IR and NMR analyses. The thermal properties of both the PEEK derivatives and their blends with PLA, the latter obtained by melt mixing with Brabender technology, were evaluated by DSC and TGA analysis, while the internal morphology of the blends was investigated by Scanning Electron Microscopy. The photo-activity of the blends of PLA with the various PEEK derivatives was assessed by EPR spectroscopy (X-band; 9GHz), monitoring their ability to generate the parent benzophenone ketyl radical upon exposure to UV radiation, a process requiring the interaction with an effective H-donor species such as e.g. PLA.
Among the three blends investigated, SPEEK (sodium salt) showed low photoactivity as a result of poor compatibility with the PLA matrix, resulting in limited interfacial interaction. Na-SPEEK plasticization with the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (4 wt%) allowed to marginally improve the quality of the PLA dispersion. On the other hand, NPEEK was found to be highly photo-active thanks to its good dispersion within PLA, with a low but stable intensity of BPK radical even 48 hs after irradiation. Finally, APEEK showed the highest photoactivity in spite of its poor dispersibility in PLA, possibly as a result of APEEK self-H-donating activity.



Photoreactivity test by EPR spectroscopy.

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P16

SYNTHESIS AND SITIMULY RESPONSIBLE PROPERTIES OF THERMAL STABLE METALLO-SUPRAMOLECULAR GELS

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Abstract

Stimuli-responsive polymers or smart polymers are high-performance polymers that change according to the environment they are in [1-2]. These type polymers are pretty popular recently and can be potentially applied increasingly in electronic, optoelectronic and medical imaging fields [3]. Among these type systems, polymeric stimuli-responsive systems have a privileged position due to their being stable and easily adaptable. Metallo-supramolecular polymers prepared through composing coordination polymers reversibly with important transition metals have important physical properties, they possess important potentials for many technological applications. Despite their importance especially in sensor and electronic fields and the increasing interest for their research in last decade, they still have many disadvantages. Their thermal durability properties being pretty low and their application processes being hard make it difficult to make use of this important potential efficiently [4]. Until today, although by using the coordination of ligand carrying molecules and different transition metal, many metallo-supramolecular polymers have been prepared and yet, the thermal durability problem in these structures still cannot be overwhelmed. Most of the synthesized structures/products decompose thermally at application temperature or slightly above. The present study has aimed to strengthen the thermal stability and sitimuly responsive properties of metallo-supramolecular polymers.

In this work, phosphosene and phenanthroline based supramolecular polymers have been designed for use in many smart polymer applications. Phosphosene groups were used to increase thermal stability and fire retardant properties of polymers. Phenanthroline group as a ligand was also used to form of polymer structure with different metal ions. Structural characterization of the prepared metallo-supramolecular polymers was carried out by elemental analysis, FTIR and NMR spectroscopic techniques. Stimuli-responsive properties of polymers were determined by UV and electro-analytical equipments. In addition to, Thermal degradation and stability of prepared metallo-supramolecular polymers were detailed studied. As a result, it has been determined that the prepared phosphosene and phenanthroline based network type supramolecular polymers have good thermal properties compare with the other linear type metallo-supramolecular polymers.

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P17

DYNAMİC STİMULİ RESPONSİVE PROPERTİES OF ADAMANTANE CONTAİNİNG SUPRAMOLECULAR GELS

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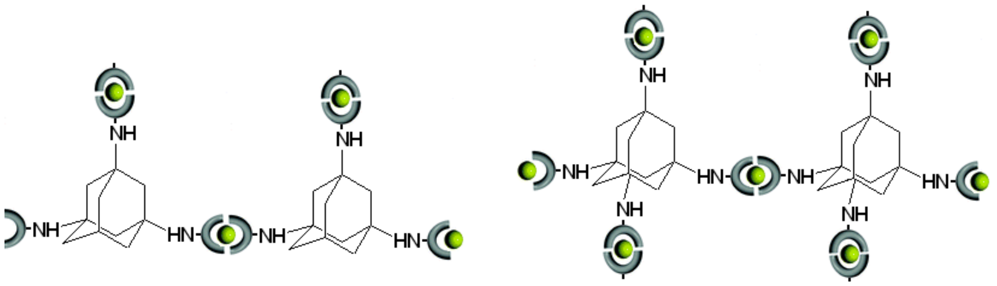
Abstract

Stimuli-responsive systems reacting to outer physical or chemical stimulator are pretty popular recently. Among these, polymeric stimuli-responsive systems have hold the privilige position due to their being stable and easily adaptable properties. Despite their importance especially in sensor and electronic fields they still posses many disadvantages. For instance thermal consistencies and durabilities are being low that make their application processes are being hard. Until today, although by using the coordination ligand carrying molecules and different transition metal, many metallo-supramolecular polymers have been synthesized and yet the thermal consistency and durability problem in these structures still cannot be overwhelmed. In this project, multifunctional and thermally stable polymeric networks were prepared in order to fulfill the gap exist in the literature by using metallo-supramolecular assembly. In order to design the molecular network adamantyl containing molecules have been chosen. Preparation of the precursors is followed by metal coordination with Zn^{2+} , Co^{2+} , Cu^{2+} and Fe^{2+} and as a result network, star polymeric metallosupramolecular assembly will be formed. Further studies will be conducted in order to gain luminescence and photoluminescence properties with Eu^{2+} , La^{2+} , Lu^{2+} and Tb^{2+}.



The authors gratefully acknowledge TUBİTAK Grant No:115R023 for support

P18

TRİAZİNE CONTAİNİNG REVERSİBLE SUPRAMOLECULAR GELS WİTH PHOTOLUMİNESCENCE PROPERTİES

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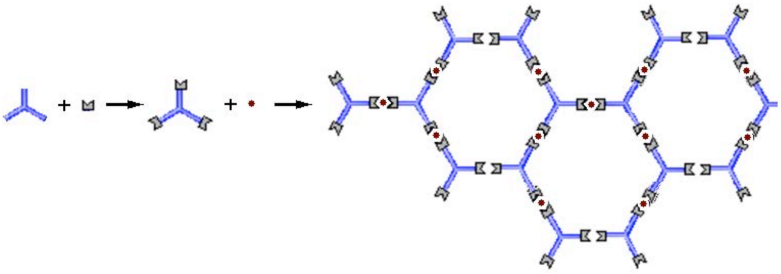
Abstract

Outstanding achievement in the synthetic chemistry of supramolecular net works has created many novel structural varieties. With the modification of novel structures with metals has come increasing interest in the properties and behavior of these assemblies. The relation of constituent components formed networks with novel properties distinct from the components themselves. Physical study of supramolecular systems informs the evolution of new dynamic structures, which express more complex supramolecular functionality. Detailed understanding of the dynamic processes becomes crucial to use supramolecular assemblies to influence reaction chemistry, selectively encapsulate small molecules, or create new nanodevices. Increasingly, the focus is on application of these molecules to other chemistry problems: selective substrate binding, trapping reactive intermediates or protecting unstable species, and influencing reaction chemistry within assembly cavities. In this project, multifunctional and thermally stable polymeric networks were prepared in order to fulfill the gap exist in the literature by using dynamic metallo-supramolecular assembly. In order to design the molecular network triazine containing molecules have been chosen. Preparation of the precursors is followed by metal coordination with Zn^{2+}, Co^{2+} , Cu^{2+} and Fe^{2+} and as a result network, star polymeric metallo supramolecular assembly will be formed.



The authors gratefully acknowledge TUBİTAK Grant No:115R023 for support

P19

PREPARATION OF ACRYLATE-BASED SILVER NANOCOMPOSITE BY SIMULTANEOUS POLYMERIZATION–REDUCTION APPROACH VIA 3D PRINTING TECHNIQUE

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Abstract

Three-dimensional (3D) printing has drawn tremendous attention from both academia and industry with its potential applications in various fields, such as the aerospace, automotive, medical, and pharmaceutical domains[i]. The integration of nanotechnology into three-dimensional printing (3DP) offers huge potential and opportunities for the manufacturing of 3D engineered materials exhibiting optimized properties and multifunctionality. In fact, the incorporation of nanomaterials, such as metal and oxide nanoparticles, into 3DP can result in improved functional and structural properties of the manufactured device, such as electrical conductivity, electromechanical/chemical sensitivity and mechanical strength. For instance, due to their excellent conductivity and antibacterial activity, metallic silver nanoparticles are increasingly used as nanofillers to fabricate nanocomposites used in a wide range of applications ranging from sensing devices to biomedical field[ii,iii].

To benefit from the combination of nanotechnology and 3DP, it is essential to improve the current understanding of the various types of nanomaterials and nanocomposites and their processing, as well as finding the proper printing techniques to build 3D systems and engineered structures.

Stereolithography (SLA) represents one of the most explored 3D techniques used for the fabrication of such devices. The general procedure for building 3D structures with SLA involves the exposure of UV-light (typically from a laser or light-emitting diode) to a photocurable resin (e.g., acrylated monomer or oligomer), which creates cross-linked regions where the light irradiates the matrix.

3D printing of nanocomposites usually concerns the mixing of *ex situ* synthetized nanoparticles in a commercially available acrylated monomer, followed by the proper printing process.

Nevertheless, in all the cases, the addition of nanofillers strongly affects the printing process: solution viscosity, light penetration depth and nanoparticles dispersion and stability[iv,v].

In this work, a novel approach for the preparation of 3D nanocomposites is proposed: the simultaneous photo-reduction of metal precursors (silver acetate) with the photo-polymerization of the acrylated monomer mixture (Ebecryl 7100, an amine functional acrylate, and PETIA, pentaerythritol triacrylate) to form a nanocomposite using the SLA technology, is presented and discussed.

The focused ultraviolet laser beam of the printer is used to locally photo-induce the reduction of silver cations, generating silver nanoparticles (AgNPs), and at the same time photo-polymerize the acrylated monomers, by means of the homolytic photo-cleavage of the photoinitiator (Irgacure 819, bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide)[vi].

The SLA printing process is used to produce 3D-printed specimens, tested for thermo-mechanical characterization (dynamic-mechanical and tensile analysis). Structure of AgNPs and microstructure of Ag nanocomposites are analysed respectively using X-ray diffraction and transmission electron microscopy. The antimicrobial and cytotoxicity tests are also performed to verify the presence of these functional properties due to AgNPs.

The result of this study shall provide a new way of developing a product for biomedical use as well as providing further rapid prototyping option to research and development.

P20

FABRICATION IN TWO-STEP MICROWAVE/ULTRAVIOLET POLYMERIZATION OF THREE-DIMENSIONAL SCAFFOLDS BASED ON NATURAL AND SYNTHETIC COMPONENTS

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Abstract

The invention of new polymeric biomaterials and scaffold fabrication techniques improve the development of tissue engineering. The structural properties of scaffolds affect cell response and have to be designed to support cell adhesion, proliferation and differentiation. In our study, the investigated scaffolds were synthesized using combined technique which includes microwave and ultraviolet-irradiation. Novel bi- and three-component polymeric hydrogels based on synthetic, 2-hydroxyethyl (meth)acrylate (HEMA/HEA) and natural, gelatin components have been produced by cross-linking polymerization. Natural polymer gelatin demonstrates great resemblance to extracellular matrix elements. 2-Hydroxyethyl (meth)acrylates upgrade mechanical properties. The structural characteristics, morphology and *in vitro* swelling tests have been performed in order to correlate the material composition with the corresponding properties. Finally, cytotoxicity detected by exposure of the hydrogel extracts to L929 cell line showed satisfied cytocompatible properties. These novel scaffolds have potential for tissue regeneration applications due to their unique, tunable architecture and physico-chemical properties.

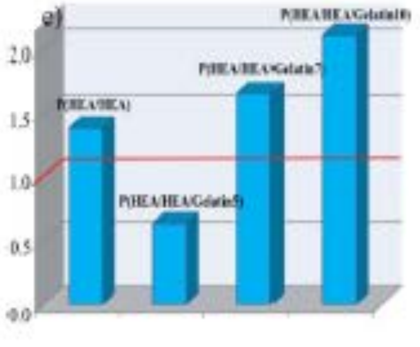

Figure 1. Effect of P(HEMA/HEMA/Gelatin) hydrogels on proliferation of L929 cell line.

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IONOMERIC POLYURETHANES COMPRISING SACCHARIDES IN THE MAIN CHAIN

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Abstract

Depletion of oil resources and deterioration of environment has driven the attention of polymer chemistry researchers to the inexhaustible plant renewable resources based biodegradable polymers.

That's why the new course of polymer science has originated, the main target of which is the obtaining of novel biodegradable materials capable to degrade under environmental conditions after the completion of their life-time. At that these materials should decompose to the harmless compounds during their degradation and must be safe for people and environment. At their best they have to decay in compost on water and carbon dioxide. Among variety of such materials, a special place in production of ecologically friendly and biologically compatible materials belongs to the polymers containing the saccharide fragments in the main chain. The most frequently used saccharides are glucose and lactose, science they serve as nourishment source for many microorganisms and may be a "recognition signal" for microorganisms-destructors. And this fact attests their use in order to impart a biocompatibility and biodegradability to synthetic polymers, thereby widening the area of their applications.

In our work we synthesized ionomeric polyurethanes containing glucose or lactose fragments in the main chain in amount of 1,5; 5; 10; 15 % (molar) calculated to polyol content. The synthesis of polymers was carried out in two stages: in the first one we obtained the mixture of two macrodiisocyatates (the first - on the basis of saccharide and hexamethylenediisocyatate and the second - on the basis of polyoxytethramethyleneglycol and hexamethylenediisocyatate in molar ratio 1:2); in the second stage we extended the saccharide-containing ionomeric olygo(urethane) with bifunctional compound (neutralized dimethylolpropionic acid) and water. The films were formed on the teflon surfaces and dried in vacuum at 60 ºC till constant weight.

It was shown that properties of obtained saccharid-containing polymers depend on the nature and content of natural component that gives an opportunity to control their life-time and degradation processes. Microbiological studies confirmed the potential biodegradability of developed polymers, displayed the microorganisms' attachment on their surface that is the first step to degradation under environmental conditions. IR-spectroscopic data showed the intense inter- and intramolecular interactions and existence of branched structure at the expense of high reactive capability of the hydroxyl groups of the saccharides. According to variety of useful properties developed materials might be used as drug delivery systems, bioimplants, contact lenses, permeable membranes, surface modifiers of synthetic polymers, polymeric detergents, ingredient of saturating compositions and interfacial compound, etc.

P22

SYNTHESIS OF EPICATECHIN-CYCLODEXTRIN BASED HYDROGELS FOR BIOMEDICAL APPLICATIONS

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Abstract

Hydrogels are a special class of polymeric networks that contain large amounts of water (~ 90wt.%) [1-2]. Because of their high water content, hydrogels are suitable for biomedical applications and biotechnological applications such as scaffolds for tissue engineering, contact lenses, bio-sensors for encapsulation and nano-carriers for drug delivery, etc [3]. Their elastic properties similar to natural tissues and their structures have flexible cavities in which body fluids can move. Thus, hydrogels can be generally used controlled drug delivery systems in medical field. Especially, they can be used to release drug, enzyme, cell and dye in biological fluids. In the literature and numerous hydrogels exist naturally and artificially. However, the scope of hydrogel applications is often severely limited by their mechanical behaviour[4]. Most hydrogels are brittle and they do not exhibit high stretchability. The present study has aimed to strengthen the mechanical properties and biocompatibility of the hydrogel structure.

In this work, biosuitable and biocompatible hydrogels have been designed for use in many biomedical applications. Basically at different rates, PEG, cyclodextrin and epicatechin as monomers were preferred. PEG groups were used with different molecular weight to increase flexibility and biodegradability. Epicatechin was used to increase biocompatibility of hydrogel. β-cyclodextrin groups was also used to cross-link in the hydrogel structure. In addition, cyclodextrin groups provide drug delivery properties. Structural characterization of the prepared hydrogels with different ratios of PEG, β-cyclodextrin and epicatechin was carried out by elemental analysis, FTIR and thermal analysis techniques. Surface properties were determined by SEM and AFM techniques. In addition to, melatonin release kinetics of prepared hydrogels were studied. As a result, it has been determined that the prepared cyclodextrin based hydrogels can be used as hormone releasing system.

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GALLIC ACID-CYCLODEXTRIN BASED HYDROGELS WITH TUNED SWELLING AND ESTROGEN RELEASE PROPERTIES

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Abstract

Cyclodextrins (CDs) are cyclic oligosaccharides composed of six, seven, or eight glucopiranose units (alpha, beta, gamma-CDs, respectively) linked by glycosidic bonds[1-2]. Their shapes resemble a hollow truncated cone with hydrophilic edges and a relatively hydrophobic cavity when compared with aqueous media. Indeed, it is the nonpolar character of their cavities that confers them unique properties, most importantly their ability to form inclusion complexes with different guest molecules [1]. Polyethylene glycol (PEG) is a synthetic polymer that has been used extensively in biomedical hydrogel systems due to its excellent biocompatibility [2]. Gallic acid (GA) is a natural polyphenolic compound, which evidences antioxidant, antibacterial, and other biological activities [3-4]. GA can be used for medicine, organic synthesis, food, agriculture, and other fields and to prepare biocompatible polymeric materials [5].

In this study, various hydrogel structures containing cyclodextrin, gallic acid and epoxy functional PEG structure at different ratios were synthesized for hormone delivery application. Structural characterization of these hydrogels was examined by FT-IR, elemental analysis and the morphological properties of the hydrogels were investigated with atomic force microscopy (AFM) SEM and EDX techniques. In addition, thermal stability and other thermal properties of the prepared hydrogel were determined by TGA, DTA and DSC analyzes. Swelling parameters, estrogen release properties and injectability of the cyclodextrin based hydrogels were tested. The hydrophilic character of these hydrogels was provided with contact angle measurements. Hydrolytic biodegradability test was applied for testing the in vitro biodegradability properties of the hydrogel. Biocompatibility of synthesized hydrogels will be tested according to the ASTM tests in the cell culture system by L929 cells.

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P24

THE ADDITIVES FOR NAVAL FILLER (YACHTING)

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Abstract

In the nautical field, the coating systems for external surface of ship play a fundamental role and they have to resist to aggressive environment and to thermal stresses.

The coating system is a protective system based on the overlap of different layers with different thicknesses. Above to the metallic or fibreglass substrate it is possible to identify at least six different layers: primer, filler, finishing filler, a second primer, undercoat and finally topcoat. The filler represents the fundamental layer from the point of view of mechanical properties: a whole category of composite materials with the first aim to fill the surface imperfections[1]. They are made up of resins, extender and additives; furthermore, they can be one-component or two-components. The two-components fillers consist of an A component (epoxy resin) and a B component (curing agent mainly based on amine group); once mixed in opportune ratios they form the filler to apply. The epoxy resins, belonging to the thermosetting materials, in the presence of suitable agents, crosslink forming products infusible, insoluble and rigid.

These materials present many problems related both to the stability in the can (with respect to their rheology and storage temperature) and the application method and related to the applied products (including their mechanical properties, corrosion and thermal stresses resistance). To improve these fillers, the additives have a remarkable role, in fact although are used in negligible quantity (between 2% and 5%) compared to the main components of the formulation, they are essential[2]. The additives used in filler are mainly of three types: rheological, defoamers and dispersant agents. Some are multi-purpose.

Rheological agents alter the deformation and flow characteristics when the material is under the stress, are often used in coatings to alter viscosity at low and/or high shear rates. A basic understanding of rheology is essential to develop acceptable flow properties in a coating system[3]. The viscosity as a function of shear applied to the coating determines many properties as stability in can, anti-settling of pigments or extenders, application performance (including sag resistance)[4]. Therefore, in the rheological agents are included several subclasses as thickeners and anti-sag agents.

Moreover in the coating are present additive used to reduce or eliminate foam. There is a difference between the term defoamer and antifoaming in fact with the first term is indicated a surface-active agent that stops the foam and breaks the bubble once it has been formed, while an antifoaming agent prevents the formation of foam so it never forms. Many defoamers are colloidal suspensions of particles that act as seeds to allow bubbles to collect and burst. The dispersant agents are additives that increase the stability of a suspension of powders (extenders and pigments) in a liquid medium, so it is clear their importance in a compound with resins and inorganic extenders[5]. The present study regards different rheological additives used to obtain high performance fillers; it was carried out by rheometer in continuous rotation and oscillatory mode, to understand their various properties and characteristics and how they work.

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P25

EFFICIENCY OF FLAME RETARDANT PLA COMPOSITIONS FOR 3D PRINTING

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Abstract

The FDM technique was used to produce flame retardant PLA specimens for cone calorimeter testing. Different flame retardant systems were compared for 3D printed and injection molded samples. All compositions (PLA + flame retardant systems) were obtained from twin screw extrusion blending. The flame retardant systems were made of ammonium polyphosphate [1] and melamine which were associated with nanoparticles such as sepiolite or organomodified montmorillonite [2]. The systems were dispersed into the whole volume for the injected molded samples but only into a limited number of layers for the 3D printed samples. The FDM technique allowed designing specimens in which a core of neat PLA was associated to various thicknesses of PLA containing the flame retardant systems. Comparisons between samples were carried out as a function of the fire retardant system and of the thickness of the coating. All samples were tested using an irradiance of 50kW/m². Heat release rate, total heat released, mass loss rate and rate of smoke release were assessed as a function of time.

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