Chemistry and Materials:

It is all about performance… and size does matter!

Gino van Strijdonck

Zuyd Onderzoek

ZUYD

Chemistry and Materials:

It is all about performance… and size does matter!

Gino van Strijdonck

Global Challenges and Sustainability

The last decades of the previous century we were confronted with pictures of dying forest. This was caused by emissions of sulfur dioxide and nitrogen oxide, which react with water in the atmosphere to produce acids resulting in acid rain. Acid rain did not only caused death of forests but also had a negative effect on coatings and paints and caused corrosion of steel and erosion of stone.

Sulfur dioxide and nitrogen oxide emission stems mainly from industrial activity, coal power plants and transportation.

Since the 1970s efforts to reduce the release of sulfur dioxide into the atmosphere led to positive results. In 1990 emissions dropped already with 40% and in 2007 the long term goals of 2010 were achieved. These results were mainly achieved by technology: introduction of flue-gas desulfurization and catalysts for vehicles. Currently we are dealing with other global challenges mainly caused by a growing population and depletion of resources.
There is certainly a need for a new socio-economic revolution driven by new technologies. As Jason Drew states in Financial Review (October, 21, 2013): "Sustainability revolution has begun". And molecular sciences will play an important role!

In 2012 the Dutch government has started the Top Sector policy. A business policy to stimulate the knowledge economy in the sectors Agri & Food, Chemistry, Creative Industry, Energy, High Tech, Logistics, Life Sciences & Health, Horticulture and Water.

The Top Sector Chemistry reported in New Earth, New Chemistry the ambition for the Netherlands to play a leading role in green, sustainable chemistry and smart materials. To that end, innovations in Smart Polymeric Materials, Process Intensification and Bio Based Economy are stimulated. For adoption and implementation of promising new technologies, especially by SME's, these technologies often need a specific development, education of students and professionals. Thus the role of Universities of Applied Sciences is pivotal.

Materials

According to Wikipedia “A material is defined as a substance that is intended to be used for certain applications”. To make a useful product, a material is selected by properties. The properties of a material are determined by its constitution and structure i.e. the properties of matter depend on which atoms are used and how they are bonded together.

Material sciences is about studying the structure of materials, and relating them to their properties. Polymers are an important class of materials. Polymers are long molecules consisting of repeating units and are the materials used to make plastics. Plastics are one or more polymers with additives. Additives are used to modify the material properties by interaction with the polymers. Well known plastics are polyesters used as textile, polyethylene for supermarket bags, polycarbonate for compact discs, phenol formaldehydes which is relatively heat and fire resistant, and thus used for e.g. insulating parts in electrical fixtures. Polyetheretherketone (PEEK) is a strong, chemical- and heat-resistant thermoplastic and is biocompatible which allows for use in medical implant applications and aerospace moldings. Polymethyl methacrylate (PMMA), also known as Plexiglas is amongst others used for “hard” contact lenses and we all know Teflon or better polytetrafluoroethylene of which heat-resistant, low-friction coatings are prepared and used as non-stick surfaces for frying pans.

There is a strong need for materials with different kind of properties and combination of properties such as mechanical, chemical, electrical, thermal, optical and magnetic properties.

With polymeric materials it is possible to design and prepare materials with the right properties. Since the fossil raw materials are almost exhausted and emissions from production have a disastrous effect on our climate there is a huge pressure to produce materials in a more sustainable way. The quality and performance of these materials, however, are most important.

Bio Based Economy

Bio Based Economy refers to an economy that is based on biomass rather than on fossil raw materials. This biomass is then converted to products such as food, chemicals, plastics, fuels etc. using techniques such as fermentation, bio refinery and pyrolysis.

There are some issues to be solved however, such as:

- *Is there enough arable land to feed mankind, supply the energy needed and supply raw materials?*
- *What about by-products such as CO_2?*
- *What is the effect of this new pharming on the environment?*

Technology development such as solar fuels and hydrogenation catalysts for CO_2 conversion would certainly make a difference.
Even though the availability of biomass and its sustainable use (e.g. as fuels) is in some cases under debate and bio based is sometimes more a goal rather than a way to sustainability, biomass, provided it is sustainably produced, can be used as a renewable raw material for the chemical industry.

Sustainability is more than bio based and bio based is more than converting biomass. Bio based research is therefore not restricted to research typically performed at the so-called green Universities. The diversity in chemical building blocks obtained from biomass after fermentation and isolation is still quite limited and research at the so called “grey universities” is needed to convert bio based building blocks to a variety of other compounds. In that respect it would be better to talk about colorful universities. But I don’t want to start a “Zwarte Pieten” discussion.

At Maastricht University, bio based alternatives for fossil based materials are developed. The role of Zuyd University is to implement these alternatives in production processes. The applied research performed in the Zuyd Beta Research Centre for Material Sciences, however, is not focused on the use of biomass (direct or after processing) to produce bio based materials. Our research is concentrated on the molecular aspects of promising technologies that contribute to a more sustainable world via an efficient way of producing chemicals and materials with outstanding performance. And disclose these technologies for SME’s.

Synthesis: Micro Flow Technology

As stated, a material is used because of its properties. The structure of a polymeric material i.e. the way in which atoms are arranged in molecules and the way these molecules are arranged, is determined by the molecular structure and the way in which it has been processed.

Once the structure-property correlation is known, the relative performance of a material in a certain application can be tested. Based on the desired properties, chemist design molecules. To test the properties of these designed molecules, they must be synthesized. Chemistry is a creative science: not only studying and describing objects or processes, but really creating new compounds. The preparation of polymers consist of preparing monomers and then converting these monomers to polymers. In an early stage of the development of new materials the main goal is to get access to these compounds. Preparation of chemicals is for centuries performed in vessels and synthetic chemist have received the same 'batch' training accordingly. Mixing and thermal issues are not considered in this phase. Current production technology is mainly based on scale-up of these lab-scale batch reactions. But a change in surface-to-volume ratio effects mass and heat transfer resulting in time consuming re-optimization steps. Furthermore, 25% of what goes in the "reactor" comes out as goods or services and 75% ends up as waste and pollution (World Resource Institute). And finally, some processes are dealing with serious safety issues at a larger scale.

The main problem in a stirred vessel is a limited heat and mass transfer and thus limited control over the reaction. The heat and mass transfer can be improved by larger surface-to-volume ratio. Similar to the blood circulation an enhanced heat and mass transfer by increasing the transfer area can be obtained by micro flow.

In a micro flow reactor, reactive components are pumped together at a mixing junction and flowed down a temperature controlled pipe or tube. Depending on parameters such as the used solutions, reactor geometry and used diameter this provides improved mass transfer (mixing) between the solutions. The heat transfer depends on the wall thickness and material, but because of the increased surface-to-volume ratio this will be improved as well, compared to batch reactors. The residence time can be controlled by the flow rate and the length of the reactor.

A more homogeneous temperature means less by-products stemming from processes at higher or lower temperature. Since the mass transfer is improved as well, reaction times are shorter not only leading to shorter and more energy efficient production processes but also to prevention of degradation products. Furthermore, further reaction of the product with starting material is prevented as well. Reduced by-product formation and unreacted starting materials by improved reaction control can simplify the downstream steps required for product isolation, potentially reducing operating costs.

Application of micro flow technology results in an easy transfer of reactions from lab-scale to production-scale by scaling out (numbering up), without needing re-optimization steps.

In general the advantages of micro flow production are:

Increased process safety
- Low reactant hold-up
- Excellent thermal & mass transfer
- Reduced plant size

Increased reaction control
- Higher reaction selectivity leading to increased yield, reduced raw material costs & downstream isolation
- Constant quality

Shorter development times
- Faster time to market
- Reduced development costs

The advantages of flow chemistry is already known to the bulk industries for decades. In the Fine and Specialty Chemical sectors, however, few processes are performed under continuous flow conditions.

Manufacturing in pharmaceutical industries is shifting from high volume block-busters to more potent lower volume Active Pharmaceutical Ingredients. The flexibility needed in combination with the search for higher resource efficiency is a driver to apply flow processes. In 2011, Dr. Janet Woodcock (FDA) predicted 'in the next 25 years current manufacturing processes are abandoned in favor of cleaner, flexible, more efficient continuous manufacturing'.

Economics

In 2006, a study by SenterNovem, Dutch Energy and Environmental Agency, showed that flow processes lead to 20-80% savings of Capital Expenditure and Operational Expenditure. This is confirmed by Ernblad and coworkers who calculated for several confidential processes a 77 % decrease in CAPEX (due to smaller and/or less equipment) and 50 % decrease in OPEX (reduced solvent usage, waste and labor) costs.

Adoption by industries

There are many drivers for industries to switch to continuous flow processes. Adoption, however, is still hampered by the fact that it competes with established, and in most cases fully written off, production infrastructure. Furthermore, the current chemists are trained using the same batch methods as used in the "old alchemy days".

So, what is needed is training of the next and current generation of chemist and engineers the skills and knowledge needed for continuous manufacturing. Even more important is the change in mindset that is needed: no more solving process problems by altering the chemistry. To help the continuous flow manufacturing revolution, novel methodologies have to be developed and case studies have to be performed with and for companies. For a successful implementation of continuous manufacturing a multi-disciplinary team having knowledge about chemistry, chemical engineering and mechanical engineering is needed.

Network on Innovation and Learning

As stated above, training and case studies are needed. To that end, the Zuyd Research Centre for Material Sciences, together with Chemtrix (a Brightlands Chemelot based manufacturer of flow equipment) and the Centre of Expertise Chemelot Innovation and Learning Labs have:

- Developed master classes (for lecturers, students and professionals)
- Developed educational tools
- Performed case studies with and for companies
- Developed a network portal

Most of this work is done in the framework of a SIA RAAK MKB subsidy in collaboration with Fontys University of Applied Sciences (Eindhoven) and Thomas Moore University of Applied Sciences (Geel, Belgium) and an Erasmus+ Life Long Learning grant from the Education, Audiovisual & Culture Executive Agency in collaboration with The Centre for Learning Sciences and Technologies (CELSTEC) of the Open University in the Netherlands, the chemistry department of the University of Hull, Provadis School of International Management and Technology (Frankfurt) and the chemistry department of Dublin City University.

The research conducted in our group is not limited to the preparation of monomers and polymers for materials but is dedicated to perform chemistry in Micro Flow in general. A few typical research cases are described.

Isobionics, a biotechnology company located at Chemelot, produces ingredients for the flavor and fragrance markets. Amongst their high quality products is nootkatone, one of the main chemical components used in grapefruit flavors. Nootkatone can be prepared by a rather hazardous oxidation of valencene. With the use of micro flow reactors this reaction can not only be conducted in a safe way, but after facile optimization, the use of MRT also provides rather clean transformation to the desired product. This selective transformation to the product does not only provide a more efficient use of the starting materials but will also be beneficial for the downstream processing steps i.e. isolate in a pure form, very important for this industry. Scale up of the process is in progress.

Caffeic acid phenethyl ester, CAPE, is a component found in the propolis of honeybee hives. Propolis is used as an adhesive by honeybees to seal gaps in these hives. CAPE is known to have anti-mitogenic, anti-carcinogenic, anti-inflammatory, anti-viral and immuno-modulatory properties. The anti-inflammatory attribute makes CAPE an interesting compound for the cosmetic industry. For test purposes, CRB Benelux B.V needed 100 gram of CAPE. In these quantities, however, CAPE is not commercially available within a reasonable period for a reasonable price. Comparison of batch production with continuous flow production led to an economically viable and environmentally benign route for production of 100 grams of CAPE using a flow process.

Cambridge Major Laboratories, Inc. is a supplier of comprehensive pharmaceutical development and manufacturing services. One of the projects involved in is the improved production of a medicine against psoriasis. An important intermediate for the synthesis of this medicine has a low overall yield. This is mainly due to a relatively low yield [~50%] of a cascade reaction that involves a Boekelheide rearrangement. The use of flow technology was highly beneficial for the efficient production of this intermediate since the yield was enhanced to over 95%. Moreover, our study has led to deeper insight in the reaction pathway.

A final example comes from our collaboration with the bio based materials group from Maastricht University. One of their projects is the conversion of bio based furans (from e.g. cellulose) to new promising building blocks such as cyclopentenones. Again it was shown that yields are generally higher using micro flow.

Many more examples (often confidential so mainly generic results) of case studies but also educational material can be found via www.microreactortechnology.eu. March, 19 we organize an event called: 'The future is in Micro Reactor Technology; safe, green and sustainable', free of charge here at the Brightland Chemelot Campus.

Challenges

Current synthetic research in the group concerns mainly the preparation of monomers and relatively small molecules. Future work will include polymer chemistry (i.e. polymerization and polymer modification) in micro flow where viscosity issues have to be handled.

Most of the research described is performed by synthetic chemistry students, lecturers and academic and industrial professionals. A next step will be to focus more on the complete process including downstream processing steps and design and dedicated production units thus integrate the chemical and mechanical engineering domain.

Secondly, fluidics and chemistry at a surface are needed to develop lab on a chip devices. Our knowledge will be used to help the Life Sciences and Health team of Zuyd with their ambition to develop diagnostic devices.

Furthermore, students and lecturers of business administration, marketing, communication and finance will be more involved in the near future.

Material Engineering and functionality: nanotechnology

With the synthesized polymers in hand we often have to add additives to modify or improve the properties or process ability of the compounds. In terms of sustainability, it can be beneficial to introduce an extra functionality.

The introduction of nanoparticles can be used to add functionality to a material or to improve the material properties. Nano stems from the greek word nanos which means dwarf and one nanometer is one billionth, or 10^{-9}, of a meter. Nanoparticles are between 1 (size of atoms: H ca. 0.25 nm) – 100 nm in size (definition used by the National Nanotechnology Initiative in the US).

To put this in perspective, humans are in the meter range. If we zoom in a thousand times, we are in the millimeter range, the typical size of e.g. greenfly. Again a thousand times smaller and we are at the micro level, 1000 nanometer, typically the size of cells. For 1 nanometer we have to zoom in another 1000 times. A DNA double-helix has a diameter around 2 nm. The smallest cellular life-forms, the bacteria of the genus Mycoplasma, are around 200 nm in length. Or from a completely different perspective: a nanometer is the amount an average man's beard grows in the time it takes him to raise the razor to his face.

At this size the amount of atoms at the surface is significant in relation to the number of atoms in the bulk of the material. The properties of nanoparticles are therefore largely due to the large surface area of the material and the properties depend on the size of the nanoparticle. This in contrast to larger particles where the properties are dominated by the bulk of the material and largely independent of their size.

Furthermore, nanoparticles can have unexpected optical properties due to quantum effects because they are small enough to confine their electrons. These properties are used in stained glass where e.g. gold nanoparticles of 25 nm are used to obtain a ruby red color. Gold particles of 50 nm in a glass matrix produce a green color. In e.g. solar cell applications, the solar absorption can be controlled by controlling the size, shape and material of nanoparticles. Because of these latter properties, the material engineering program focused on nanoparticles is conducted in close collaboration with the solar energy group of Zeger Vroon. One of our main projects in this program is UV absorbing nanoparticles. To prevent materials from the damaging effects of UV light UV absorbing organic compounds are added to coatings, plastics and cosmetics. In some aspects inorganic absorbers have superior properties: they do not migrate and are more stable. Applications, however, are hampered by the high concentrations needed and scattering of light. In principle these problems can be solved by using nanoparticles. These particles, however, are difficult to produce and depending on the application need to be surface modified to disperse in a matrix. Furthermore, these particles show a photo catalytic effect i.e. light induced formation of material damaging radicals.

With financial support of SIA (Raak Pro), Kriya Materials, DWI an der RWTH Aachen, TNO, Nanohouse and Zuyd University of Applied Science are developing several surface modified nanoparticles and doped particles to diminish the photocatalytic effect of nanoparticles and improve the dispersion in several matrices. One of the applications is a coating for solar cells to improve the life-time.

Although we are making progress in hampering the photocatalytic effect, this still needs improvement. Promising results, however, are obtained in terms of refractive index which has resulted in a demonstrator coating for anti-reflective applications and recently we have used Zink oxide nanoparticles for down conversion i.e. transforming higher energy photons which are not converted to energy in a solar cell to lower energy photons which can be converted to electricity.

As with microflow, nanoparticle technology is not widely used yet and both education and specific applied research is needed. Thus also in this program a master class was developed. Furthermore, inorganic chemistry and nanotechnology are now included into the curriculum of Zuyd University.

Challenges

The nanotechnology research at Zuyd is mainly focused on the use of inorganic nanoparticles (nano in 3 dimensions) and coatings (nano in 1 dimension). Nanotechnology can be defined as the engineering of functional systems at the molecular scale. This also includes building functional systems from molecular components which assemble themselves chemically by principles of molecular recognition. This principle, which is ubiquitous in nature, is also important for the properties of materials and is one of the key issues in 3D printing, our 3rd key-technology.

Processing: 3D printing

When we have prepared a polymer, this polymer needs to be processed to improve or modify the properties and to form the material into the desired shape. Forming and shaping can be performed in the solid state or in the liquid state (molding).

Many of the shaping processes, especially in the solid state, includes a “removal” process that eliminates portions to achieve a desired shape. Opposed to these subtractive manufacturing methodologies it is also possible to make objects from 3D model data joining or adding materials, usually layer upon layer. Recently, these so called additive manufacturing or 3D print techniques receive broad attention.

The main asset of 3D printing is the almost unlimited designer freedom. 3D printing can be performed with a variety of materials and different deposition techniques. Some spectacular results in 3D printing have been achieved in the art, medical and industrial domains. 3D bio-printing has already been used for the generation and transplantation of several tissues, including multilayered skin, bone, and heart tissue. Defense manufacturer Aerojet Rocketdyne introduced a small, 3D printed rocket engine. These successes, however, are mainly obtained with living biological materials or metals in applications with a high added value. On the other hand, using polymers for printing results in low quality products at a very slow production rate.

Quality issues and production speed are met with all current polymer 3D print technologies but are most prominent in Fused Deposition Modelling. This technology is used most often for home printers. In FDM the object is produced by extruding small drops of molten material. To form a certain shape the material hardens immediately to form layers. A string (filament) of material is supplied to an extrusion nozzle head. The nozzle head heats the material and can be moved in all directions.

Since the material has to solidify fast, the molecules are more or less frozen in a random orientation. Especially for large polymers this means that they do not have the time to entangle with the next layer. This results in a layered structure with welds and inherent mechanical weakness.

In the “frozen” state there is still some mobility. Driven by intramolecular interactions the molecules will use this mobility to get organized in lower energetic state and partly crystallize. In the crystalline state, however, the molecules occupy a different amount of space thus leading to the loss of shape in time. For polylactide acid (PLA), one of the most used (biobased) polymers in FDM, this process can take up to months.

The current class of polymers used are not developed and optimized for 3D printing. To improve the performance of polymers in FDM, dedicated research is needed.

To this end Brightlands Chemelot Campus, University of Maastricht, LIOF, Fablab Maastricht, CHILL and the Zuyd Research Centre for Material Siences started the Additive Manufacturing Materials Centre with financial support from Limburg Economic Development (LED). The main goal of this centre is to develop new, good performing materials for 3D print applications.

The board of Zuyd University of Applied Sciences recognizes the importance and huge impact of 3D printing and granted additional financial support to this research theme.

At the moment several projects with companies are performed for example the use of the biobased polymer Bionate for biomedical applications with DSM Biomedical.

A consortium of Zuyd, Maastricht University, Fontys, CHILL, 3D printer developer and producer Ultimaker, API an applied polymer research institute and Xilloc Medical a developer and producer of implants in collaboration with plastic suppliers DSM engineering plastics, DSM biomedical and Corbion Purac and rapid prototyping service provider Materialise started a project on the molecular design of quality materials for 3D printing. An application for financial support from SIA is submitted.

The focus of this project is to get insight in the effect of molecular structure, molecular weight, molecular weight distribution, nucleating agents, blends etc. on the properties (e.g. crystallization rate) of plastics and their performance in FDM. The use of secondary (supramolecular) interactions between molecules will be explored to avoid the mechanical weakness between the layers of a printed product.

To fully exploit the possibilities of 3D printing, chemists, mechanical engineers, software developers and others have to collaborate. Furthermore the technologies are applied in several domains such as health, care, built environment and will have an impact on many other domains such as business. In the near future collaboration with these disciplines both within Zuyd as with external partners will be pursued.

Research Model: Communities for Development

Because it is all about performance I would like to share with you how we organize our research, combine it with education of our students and with professionalization of the lecturers and secure the quality and the involvement of companies.

Our research is performed in the laboratories of Chemelot Innovation and Learning Labs. Students, in the role of starting professionals, work together with an experienced professional under supervision of a coach on an applied research or innovation question from companies. The main and common goal is to answer this question. The experienced professional and coach can be lecturers, professionals form companies and universities or professionals from CHILL. This model is very similar to the common university research structure, where students work together with Ph Ds and post-docs on a daily basis and are supervised by a professor.

Our starting professionals are mainly students Applied Sciences from Zuyd, working on a mandatory research minor and students from the local vocational education institutes Leeuwenborgh and Arcus. The number of students from other departments and other institutes is slowly increasing.

As the assignment is central in the CfD (sub)project group, all participants can learn from each other in a real-life setting and have to perform their "natural" role. When needed, advice, knowledge and equipment can be obtained from the network of the participants, CHILL and the Brightland Chemelot Campus. An independent person assesses the process of the CfD and the performance of its members. Thus the CfD being a tool for education and professionalization.

The assessor and the students are provided by the educational institutes. The experienced professional and coach can be from the educational institute a company or a university but is paid with external means i.e. a company (in kind or in cash), a subsidized project, or a combination of these two, which is often the case. Also other resources (materials, equipment) are funded in this way.

Conclusion

In conclusion, the Research Center for Material Sciences of Zuyd University of applied sciences is engaged in synthesis, polymerization and material engineering processing and testing with a focus on 3 technologies: micro flow, nanoparticles and 3D printing.

Often bio-based starting compounds will be used but a more sustainable product can also be achieved by combining functionalities, enhance life time, close material cycle or use materials and energy in a more efficient way.

A plethora of applications have our interest but there is special attention for the regionally driven Zuyd spearheads Care & Technology, Life Sciences (Health, monitoring devices) and Sustainable Built Environment & Energy.

The core competences needed are synthetic chemistry, polymer chemistry and material engineering (plastics), the involvement of chemical engineers, mechanical engineers and analytical chemist is, however, indispensable.

CfDs and the presence of CHILL at the Brightland Chemelot Campus ensures the feasibility and the quality of research at a University of Applied Sciences, where academic research is brought to the market and this gap is finally clos. Furthermore the sharp border between learning and working or student and professional has faded and Life Long Learning lost its wooly image.

I hope I have shown you that Chemistry and Materials is all about performance:

Cleaner and safer production with micro flow

Smart, combined functionalities, e.g. with nanoparticles

Materials must have highly quality properties. Because of safety reasons I wouldn't like to have my car pimped with a 3D printed bumper...yet!

But also students, lecturers and researchers have to perform as professionals and that means more than having knowledge and skills. And there is always more to learn.

For a good performance sometimes size does matter, and large is not always better: micro flow, nanotechnology. We will help to bring these potentially sustainable technologies to the users.

For the future of our children.

Bibliography

Micro Flow

C. Wiles, *Continuous Manufacturing – Producing More with Less*, White Paper obtainable via ***www.chemtrix.com***

A. Pohar and I. Plazl, *Process Intensification through Microreactor Application*, Chem. Biochem. Eng. Q. 23 (4) 537–544 (2009)

I. R. Baxendale, *The integration of flow reactors into synthetic organic chemistry*, J. Chem. Tech. Biotech. 88 (4) 519-552 (2013)

V. Hessel (Ed.), A. Renken (Ed.), J. C. Schouten (Ed.), J. Yoshida (Ed.), *Micro Process Engineering: A Comprehensive Handbook*, Wiley-VCH (2009)

D. M. Roberge, L. Ducry, N. Bieler, P. Cretton and B. Zimmermann, Microreactor Technology: *A Revolution for the Fine Chemical and Pharmaceutical Industries?*, Chem. Eng. & Tech. 28 (3) 318–323, (2005)

P. Watts, C. Wiles, *Micro reactors, flow reactors and continuous flow synthesis*, J. Chem. Res. 36 (4) 181-193 (2012)

Nano Technology

K. E. Drexler, Engines of Creation: *The Coming Era of Nanotechnology*, Doubleday (1986)

M. Niederberger, G. Garnweitner, J. Buha, J. Polleux, J. Ba, N. Pinna, *Nonaqueous synthesis of metal oxide nanoparticles:Review and indium oxide as case study for the dependence of particle morphology on precursors and solvents*, J. Sol-Gel Sci. Techn. 40 (2-3) 259-266 (2006)

A. Becheri, M. Dürr, P. Lo Nostro, P. Baglioni, *Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers*, J. Nanopart. Res. 10 (4) 679-689 (2008)

X. Chen, S. S. Mao, *Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications*, Chem. Rev. 107 (7) 2891–2959 (2007)

Additive Manufacturing

J. Excell, S. Nathan, *The rise of additive manufacturing*, The engineer. ***www.theengineer.co.uk/in-depth/the-big-story/the-rise-of-additive-manufacturing/ 1002560.article***, retrieved 2015-02-02

C. H. Amon, J. L. Beuth, L. E. Weiss, R. Merz, F. B. Prinz, *Shape Deposition Manufacturing With Microcasting: Processing, Thermal and Mechanical Issues*, J. Manuf. Sci. Eng. 120(3), 656-665 (1998)

Wohlers Report 2014, 3D Printing and Additive ManufacturingState of the Industry

B. A. G. Schrauwen, R. P. M. Janssen, L. E. Govaert, H. E. H. Meijer, *Intrinsic Deformation Behavior of Semicrystalline Polymers*, Macromolecules 37 6069-6078 (2004)

R. H. Boyd, *Relaxation processes in crystalline polymers: experimental behaviour-a review*, Polymer 36 (3) 323-347 (1985)

S. Murphy, A. Atala, *3D bioprinting of tissues and organs*, Nature Biotech. 32 (8) 773–785 (2014)