‘SMART POLYMER MATERIALS’ AT TNO

RESPONSIVE MATERIALS & COATINGS
FUNCTIONAL INGREDIENTS
THIN FILM TECHNOLOGY
STRUCTURAL RELIABILITY
MATERIALS FOR INTEGRATED PRODUCTS
‘SMART POLYMER MATERIALS’ AT TNO

RESPONSE MATERIALS & COATINGS

HIGH-TECH COATINGS
– Bio-based and self-healing coatings
– Advanced coatings for wind turbine blades
– Hydrophobic coatings to prevent liquid loading in gas wells
– Hydrophobic coatings for the improved performance of wafer steppers

SENSOR MATERIALS
– Chemical sensing using responsive composite coatings in oil and gas wells
– Low-cost, mass-manufacturable sensors using nano-imprint lithography

ENCAPSULATION & CONTROLLED RELEASE
– Stabilisation of salt hydrates for compact thermal energy storage
– Controlled release of biocides for various anti-fouling applications in the built environment

LIGHT MANAGEMENT
– Nano-structuring of polymer composites for the use in optical waveguides
– Enhanced in- and outcoupling of light in optical devices, such as solar cells, LEDs or sensors

INNOVATIVE POLYMER COMPOSITES
– Composite hydrogels featuring temperature responsive gelation behaviour
– Materials for additive manufacturing
– Improved cement for zonal isolation using dedicated polymers

FUNCTIONAL INGREDIENTS

COATINGS
– Carbohydrate-based alternatives for polyacrylates
– Carbohydrate based polyacrylate alternatives
– Thickening additives based on biopolymers
– Cross-linked particles as an alternative to latex
– Anti-corrosion additives for water-based paints based on carbohydrates
– Application of lignin and derivatives in coating formulations

ENCAPSULATION
– Food grade water barriers to reduce water migration in food products (dual barrier)
– Incorporation of active ingredients in a biopolymer cross linked system (Bioswitch®)

THIN FILM TECHNOLOGY

SPATIAL ATOMIC LAYER DEPOSITION

MOLECULAR LAYER DEPOSITION

PLASMA PROCESSING
– Plasma etching/cleaning
– Surface activation
– Plasma-assisted grafting
– Surface polymerisation.

STRUCTURAL RELIABILITY

CEMENT-BASED BUILDING MATERIALS (CONCRETE, GEOPOLYMERS, MASONRY)
– Improved cement for zonal isolation using dedicated polymers
– Upgrading waste streams like bottom ash to new building materials

BITUMINOUS ROAD MATERIALS (ASPHALT)
– Improving the durability of bituminous road materials by adding fibre systems
– Replacing bituminous road materials by lignine-based materials
– Improvement of (self-)healing properties in road construction materials

MATERIALS FOR INTEGRATED PRODUCTS

MULTI-SCALE MODELLING

ELECTRONIC MATERIALS
– Flake/particle filled adhesives for electronic applications
– Molding compounds for automotive electronics
– Piezo-electric material binders for smart product manufacturing

LIGHT MANAGEMENT
– Material solutions for OLEDs
– Optimisation of anti-reflective coatings
– Sensor integration design
The Dutch chemical industry has recently defined two ambitions. First, in 2050 the Dutch chemical industry wants to be in the top 3 countries that develops and produces ‘smart materials’. Currently, the Netherlands has one of the lowest added values on the chemical industry in comparison with the surrounding countries. Therefore, the second ambition is to double the added value of the Dutch chemical industry by 2030.

TNO wants, can and definitely should contribute to these ambitions. Therefore, the theme ‘Sustainable Chemical Industry’ of TNO presents in this document the activities and competencies in the field of ‘smart polymer materials’.

Currently, 5 research groups at TNO are active in materials research. These are ‘Responsive Materials & Coatings’, ‘Functional Ingredients’, ‘Thin Film Technology’, ‘Structural Reliability’ and ‘Materials in Integrated Products’. The respective competencies and research topics are listed below. These topics are further illustrated in the remainder of the document.
EXPERTISE GROUP: RESPONSIVE MATERIALS & COATINGS

The core competency of RM&C is to create novel functionalities and polymer materials by physical and chemical structuring at the micro- and/or nano-scale.

HIGH-TECH COATINGS

BIO-BASED AND SELF-HEALING COATINGS

TNO is working on different fronts towards bio-based, self-healing coatings. Evaluation of bio-based monomers involves in the first place their polymerisation into suitable resins. Second, the resin is formulated into a coating. The properties of the coating and herewith its application are finally evaluated and compared to existing coating materials. The goal of the work is to either replace common coating materials or to develop new materials with improved properties.

Additionally, TNO has developed bio-based coatings with self-healing properties. The self-healing effect enhances the lifetime of coatings and can also enable adhesives with reversible bonding-debonding properties. Two different approaches are available to achieve the healing effect. The first approach exploits the furan functionality of the bio-based coating for reversible crosslinking. A Diels-Alder reaction is used for the reversible crosslinking of furan with maleimide compounds. The chemical bonds break at higher temperatures and crosslink again when the material cools down. This is a typical example of a bio-based polymer exhibiting new functionalities which traditionally could not be achieved. The second approach, involves the micro-encapsulation of linseed oil and the subsequent incorporation in coating materials. Linseed oil is a bio-based material, which has the capability to polymerise when it is exposed to air. The microcapsules when the coating is damaged. The oil flows in the scratches or microfractures of the coating, is exposed to the air, polymerises and hereby heals the coating.

In addition, TNO initiated three research programs (CHAPLIN, BIO AROMATICS and GAIA) to investigate the extraction and use of bio-based resources for the development of new materials. The three research programs respectively investigate the use of lignin, bio aromatics and compounds derived from algae. This topic requires expertise in biology, chemical engineering, organic chemistry, polymer synthesis, characterisation and microencapsulation.

ADVANCED COATINGS FOR WIND TURBINE BLADES

Nanostructuring of wind turbine blades is advantageous for the energy yield due to a more effective rotation. At the same time nanostructuring reduces wear and biofouling. This is realised by the introduction of nanoparticles in the coatings. Thermoplastic composites are also of high interest for windblades as they enable larger blades with reduced weight. Additionally, the polymer composites will be protected with a thermoplastic coating to generate sufficient durability.

HYDROPHOBIC COATINGS FOR THE IMPROVED PERFORMANCE OF WAFER STEPPERS

Immersion lithography is a technique developed by ASML to pattern/structure silicon wafers at a high resolution. In this technique transport of water is of crucial importance for contamination control, and production speed. The coatings developed by TNO enable fast water transport due to their high hydrophobicity and stability in the extreme environment required for this high-end fabrication process. Synthesis and coatings application were crucial for the industrial acceptance of such coatings.

Hydrophobic coatings.
SENSOR MATERIALS

CHEMICAL SENSING USING RESPONSIVE COMPOSITE COATINGS IN OIL AND GAS WELLS

Distributed chemical sensing (DCS) technology is being developed by TNO in collaboration with Shell. The aim is continuous monitoring of the chemical composition in oil and gas wells. The principle for DCS is a combination of fiber optic technology with responsive coatings. The principle so-far has been demonstrated for the detection of H₂O, CO₂, H₂S and brine under extreme conditions. The so-called Fibre Bragg gratings (FBG) are used to detect changes in strain in the optical fibre. Novel polyacrylate and polyimide coatings have been developed that swell when they come in contact with specific analytes. Swelling of the coating induces strain along the optical fibre, resulting in detection of the analytes. Durability and adhesion of the coatings at the down-hole conditions is essential to ensure long-term performance and is achieved by a combination of robust chemistry and the suitable processing conditions. Additionally, the optical fibres are packaged and protected from the harsh conditions in the oil and gas wells (high temperatures, pressures and salinity). Therefore, TNO has developed a special protective hydrogel packaging for the optical fibres that allows permeation of the analytes, but is impermeable for oil and impurities. In summary, such a development requires intimate knowledge of enhanced oil and gas recovery and expertise in the field of optical sensing using FBG technology, responsive polymer composites and protective coatings.

The Gas exposure box developed by TNO in which the functionality of coated fibres can be evaluated.

LOW-COST, MASS-MANUFACTURABLE SENSORS USING ROLL-TO-ROLL NANO-IMPRINT LITHOGRAPHY

TNO is developing low-cost, mass-manufacturable, nano-structured, large-area multi-parameter sensors for the use in environmental and pharmaceutical applications. Currently, utilisation of multi-parameter sensing is hindered by the lack of low-cost and, highly reproducibility fabrication methods for nano-structured surfaces. TNO addresses these challenges by developing nano-imprinting manufacturing methods for texturing of large area polymer films. Scientific work includes the development of new optically functional polymer materials, multilayer nanophotonic sensor structures, materials for large-area nano-imprint fabrication and chemically responsive coatings. High refractive index transparent polymer composites are developed specifically for this topic, which is achieved by dispersing high refractive index nanoparticles (TiO₂) with tailored polymers used for nano-imprinting. Additionally, chemically responsive coatings are developed that change their optical properties when exposed to particular analytes. In particular, a chemical sensor for formaldehyde has been developed. In summary, this topic requires expertise in a variety of fields, such as of roll-to-roll imprint fabrication processes, optical sensing, photonic nanostructures, polymer composites and chemically responsive polymers.

ENCAPSULATION & CONTROLLED RELEASE

STABILISATION OF SALT HYDRATES FOR COMPACT THERMAL ENERGY STORAGE

Dehydration and subsequent rehydration of salt hydrates allows the compact storage and release of thermal energy. Stabilisation of the salt hydrate is necessary to prevent deformation and maintain efficient heat transport in and out of the material. Our broad knowledge of encapsulation processes led to the formation of encapsulates with different sizes and geometries, such as matrix-type, multi-core and core-shell particles. The encapsulation with polymers of different water-permeability allowed careful optimisation of the hydration behaviour and consequently the thermal properties of the final material. The aim is to use the developed material for compact heat storage in the built environment.

MERITS EU

ETP Materials

Micro-encapsulated calciumchloride hexahydrate (CaCl₂ · 6H₂O).

CONTROLLED RELEASE OF BIOCIDES FOR VARIOUS ANTI-FOULING APPLICATIONS IN THE BUILT ENVIRONMENT.

Biodieses are used in many finishing and building materials, such as coatings or plaster, to reduce the growth of algae or fungi. Unfortunately the use of biocides, and the emissions they produce, can be hazardous for human health as well and therefore should be limited. The
encapsulation of biocides onto inorganic high-aspect ratio particles (clay) results in a controlled and sustained release of biocide in the building material, in contrast to the burst release for not-encapsulated biocides. This leads to more efficient use of the biocide and a prolonged lifetime of building materials. The combination of our broad expertise on encapsulation and clay allowed us to develop a novel encapsulation process. Crucial for this encapsulation process is the chemical modification of the clay’s surface. Furthermore, adjusting the modification allows to control the release profile of the biocide in the building material. Finally, knowledge on the dispersion of (micro/nano-)particles in polymer materials allowed incorporation of the biocide-clay composites into building materials.

**LIGHT MANAGEMENT**

**NANO-STRUCTURING OF POLYMER COMPOSITES FOR THE USE IN OPTICAL WAVEGUIDES**

The target applications for this topic are optical waveguides and photonic structures for the manipulation and efficient guiding of light in, for example, photonic integrated circuits (PICs) and optical interconnects. This technology may be applied for data communication, sensors as well as multimedia devices. Easy processable, transparent and nano-imprintable polymers are developed for the replacement of conventional IC materials. The success of these materials for the use in optical waveguides lies in the careful control of the refractive index of the waveguide and the surrounding material. Structuring of this polymer into optical waveguides and photonic structures is done via nano-imprint lithography. Therefore, the polymer material needs to meet certain requirements for the imprinting process, such as suitable wetting properties, viscosity and UV-curability. The photonic crystalline structures will be used as method for efficient light bending. In summary, this topic requires knowledge and expertise of optics, polymer chemistry and physics, nano-imprint fabrication.

**INNOVATIVE POLYMER COMPOSITES**

**COMPOSITE HYDROGELS FEATURING TEMPERATURE RESPONSIVE GELATION BEHAVIOUR**

Inorganic high-aspect ratios nanoparticles (clays) are functionalised with temperature-responsive, water-soluble polymers. The used polymer is poly(n-isopropylacrylamide) (pNIPAM), which exhibits a so-called lower critical solution temperature (LCST). Above the LCST the polymer becomes insoluble in water. However, the combination with the solid nanoparticles lead to a material that gels above the LCST. This can be used as a temperature switch to control the viscosity. The properties of the hydrogel (switching temperature, gel strength and osmotic pressure) can be tuned via the monomer composition and the polymer structure. For example, hydrogels composed of a block copolymer structure, in contrast to random copolymers, exhibit a significantly higher osmotic pressure while maintaining their LCST. The temperature responsive hydrogels are used in a variety of applications, such as back pain reduction, enhanced oil recovery and fire extinguishing. First, the hydrogels are used for regeneration of the intervertebral disc. The hydrogel itself can initially be used as a replacement for the intervertebral disc and additionally the hydrogels can be used for loading and controlled release of drugs to enhance recovery. Second, the hydrogels can be used for delayed gelation behaviour for enhanced oil recovery (flow diversion). Third, the temperature responsive gelation improves the efficiency of fire extinguishing.

**SMART POLYMERIC MATERIALS AT TNO**

**ENHANCED IN- AND OUTCOUPLING OF LIGHT IN OPTICAL DEVICES**

Enhanced in- and outcoupling of light is relevant for several applications. However, the main application is to enhance light harvesting in thin film, next generation solar cells. TNO works on so-called CIGS solar cells, which in principle allow high efficiency in combination with thin films. The main advantage of thin solar cells are their relatively low costs. On the other hand, the disadvantage of thin films are the poor adsorption of light. Other applications for which enhanced in- and outcoupling is relevant are light emitting diodes (LEDs), optical sensors and anti-reflective coatings. Improved light-management is achieved by structuring the material on the nano-scale. This can be achieved by the incorporation of plasmonic nanoparticles hollow particles or nano-imprint lithography. In summary, this topic requires expertise in optics, nanoparticle synthesis and dispersion, polymers and nano-imprint lithography.

**MATERIALS FOR ADDITIVE MANUFACTURING**

In additive manufacturing, products are prepared from a digital model without using a mold, in a layer-by-layer fashion. Different processes can be used, such as powder bed fusion, material jetting or stereo-lithography. In the latter process, a liquid resin is converted into a solid product by selective photo-polymerisation. By varying the resin composition, both the process speed and the material properties of the product can be tuned. Research has been focused for instance on creating flexible materials, temperature-resistant materials or tough and biocompatible materials for use in dentures. Apart from polymer products, this process...
can be used to create composite or ceramic products. In this case, ceramic particles are dispersed into the photo-curable resin to be used in the process. The resulting composite product may be converted into a fully ceramic product by debinding and sintering. Optimising resin formulation, including optimising the dispersion of the ceramic particles, is essential to ensure good processability and good product performance. In recent projects, research has been focused on alumina products as well as piezoelectric materials. In summary, this topic requires expertise with additive manufacturing, optics, ceramics, polymer and colloidal chemistry, coating technology and detailed material characterisation.

**EXPERTISE GROUP: FUNCTIONAL INGREDIENTS**

The Functional Ingredients research group offers expertise and knowledge aimed at new applications of biopolymers for food and non-food applications. The core competence is the chemical modification of biopolymers in order to alter the properties of biopolymers.

**COATINGS**

**CARBOHYDRATE-BASED ALTERNATIVES FOR POLYACRYLATES**

TNO has developed an oxidation technique using tetramethyl pypiridine-N-oxide (TEMPO), which allows the selective functionalisation of primary hydroxyl groups of polysaccharides into aldehydes or carboxylic acids. The selectivity arises from the steric hindrance of the TEMPO molecule towards the other hydroxyl groups. Besides the selective oxidation, other benefits of this method are a high reaction rate and yield. Additionally, high molecular weight polysaccharides can be used with this method and only minor degradation of the polymer chain is observed. This technology has been licensed to a spin-off company called Glycanex.

Since quite large molecular weights (e.g., over 700 kDa) are feasible with this approach, polyacrylate-like products were made and tested. For example, a super absorbing biopolymer with typical polyacrylate characteristics, such as high water uptake, has been developed for diapers. Quite a number of polysaccharides are able to bind water and form hydrogels. This effect is used in several food products, such as sauces. Modified polysaccharides can also be used as a viscosity modifier to aqueous paints/latexes. The rheological properties (e.g., viscosity, thickening efficiency) can be tuned, as mentioned above, by the selective introduction of carboxylic acid groups on the primary hydroxyl group of the saccharide units and simultaneously controlling the molecular weight.

In contrast to the hydrophilic modification, carbohydrates can also be hydrophobised via an esterification reaction. This reduces the water sensitivity of the final materials containing the modified polysaccharides.

Low water sensitivity is for example important in protective coatings.

TNO has devoted time and effort on crosslinking biopolymers (carbohydrates and proteins) into three dimensional networks. In this way micron-sized particles are obtained, which are able to absorb and bind water (microgels). The crosslinking can be achieved through the reaction of di-epoxides or sodium trimethyl phosphate under alkaline conditions. The concentration of crosslinker dictates the crosslinking density and herewith the properties of the formed microgel particles. In this way it is possible to create matrices with different characteristics with regard to e.g. water absorbance and pore size. A typical application for these particles are e.g. in latex gloves. The particles will form a gel like film e.g. between the skin and latex resulting in an efficient barrier for chemicals that may leak out of the latex gloves. Other applications that can be envisioned is in wall paints and paper coatings.

The hydrophilic modification (selective oxidation), hydrophobic modification (esterification), control over the molecular weight and crosslinking provides an extensive toolbox to tune the properties of carbohydrate and provide a bio-based alternative for conventional polyacrylates. This topic requires the combined knowledge of biopolymer properties, chemistry and processing. Additionally, knowledge of the typical polyacrylate applications is needed.

**Shell Bi-lateral collaboration**

**PENROSE 3 Co-financed collaborations**

**IMPROVED CEMENT FOR ZONAL ISOLATION USING DEDICATED POLYMERS**

Zonal isolation is required for the integrity of the bore hole in oil and gas recovery. A lot of well bores show failure of zonal isolation and this poses severe environmental and health risks since hydrocarbons or previously injected fluids leak to the surface or into nearby aquifers. A cement sheath is placed around the leak to the surface or into nearby aquifers. Hydrocarbons or previously injected fluids may result in environmental and health risks since isolation and this poses severe lot of well bores show failure of zonal isolation is required for the integrity of the bore hole in oil and gas recovery. A cement-polymer composite sheath are must be taking dedicated polymers. This ultimately results in a cement-polymer composite sheath having less defects. Care must be taken with the selection of the polymers. Important aspects are: compatibility with cement mixture and cement setting chemistry, long time temperature stability and processability. In summary, this topic requires profound knowledge of enhanced oil and gas recovery, building materials and polymer chemistry and physics.

**Glycanex**

Improved cement using dedicated polymers.
CARBOHYDRATE-BASED ANTI-CORROSION ADDITIVES FOR WATER-BASED PAINTS

TNO has participated in a large consortium of companies with the purpose of developing new carbohydrate-based ingredients aimed at corrosion protection. Chemical modification of the used carbohydrates was needed to ensure optimal compatibility with the water-based paint and secure the anti-corrosion effect. The following chemical modification were performed. First, the molecular weight is reduced to minimise the effect on the rheological properties of the paint. Second, carboxylic acid groups were introduced through oxidation of the naturally present hydroxyl groups. This resulted in improved adhesion to the metal surface and increased affinity towards the metal ions, which is required for the anti-corrosion effect. Third, minor hydrophobation of the polymer via esterification was necessary to reduce the water sensitivity of the final coating. The proposed mechanism behind the anti-corrosion effect is the complexation of the Fe$^{2+}$ ion with carboxylic acid groups. The insoluble complex then forms a protective layer on the metal surface. The developed carbohydrate-based anti-corrosion ingredients were added in 0.5 weight percent to the final formulation. Application tests have performed on a dry-dock in Delfzijl (see picture below). The results of this work have been published and patented. In summary, this topic requires profound knowledge about bio-polymer properties, chemistry and processing. Understanding of corrosion pathways and typical polyacrylate formulations is also required.

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APPLICATIONS OF LIGNIN AND DERIVATIVES IN COATING FORMULATIONS

Lignin is next to cellulose one of the most abundant organic raw materials produced by nature. The polymer is compared to cellulose hydrophobic and functions mainly as an adhesion between the cellulose fibers. The major producer of lignin and lignin derivatives is the paper and pulp industry. During the production of cellulose fibers lignin needs to be removed and the most predominant process for lignin removal is Kraft bleaching using sulfite. The lignin recovered from this process contains sulfur which hampers the use of Kraft lignin in many applications. TNO together with an industrial partner started an initiative whereby new application routes for lignin are going to be developed based on sulfur-free lignin. This new type of lignin is becoming more available since the introduction of new extraction methods such as organo-solv (hot ethanol-water mixtures), caustic and acid-based extraction (e.g. Klason). All these new extraction processes produces sulfur-free lignin already on pilot scale and soon to be on industrial scale. Sulfur-free lignin has interesting properties such as suitable melting behaviour, which allows efficient polymer processing. The absence of sulfur allows modification using transition metal assisted catalysis. Moreover, the aromatic rings allow radical initiated cross-linking. Together, this allows a broader application area than sulfur-containing lignin, especially for coatings such as primers and lacquers. Currently TNO and industrial partners are organising a consortium including producers, processors and end-users to valorise the concept.

Molecular structure of lignin.

Food Grade Water Barriers to Prevent Water Migration

TNO has developed over the last decade a water barrier coating technology for food components. Using and subsequently adapting models from the industrial coatings industry combined with a translation towards food ingredients TNO is able to develop custom made food grade coatings which act as a water barrier between a substance with a high water activity (e.g.
a filling) and a substance with a low water activity (e.g., a cake). In the last decade several projects have been successfully executed and custom made coatings have been developed. It shows the versatility of the technology. The appearance of the coatings vary from transparent to translucent and are able to withstand baking conditions (mainly high temperatures). They always consist of a blend of food grade components. Example hereunder shows the technology wherein a biscuit is coated and formulated in a yogurt. The biscuit stays crunchy for over one month. The technology is generic and can be used in other research areas where the use of bio-based materials is an item or where better barrier properties are required, such as in the microencapsulation of sensitive food ingredients. For example, using a combination of hydrophobic biopolymers and food-grade crystalline nanoparticles a coating formulation was developed with good water as well as oxygen barrier properties. This material was used for the microencapsulation of oxygen-sensitive food oils, leading to an improved storage stability. Keeping the encapsulated ingredient in a humid environment (90% RH) for several months did not lead to significant oxidative degradation. Combined knowledge on bio-polymers, food products, water migration and barrier coatings is necessary.

**ENCAPSULATION OF ACTIVE INGREDIENTS IN A CROSSLINKED BIOPOLYMER MATRIX**

TNO has developed a release on command technology nicknamed BioSwitch®. It consists of a cross-linked biopolymer matrix in which an active ingredient is trapped. Active ingredients vary from large proteins (15 kD and higher), colourants, anti-microbial compounds etc. During the development several variations have been developed including the use of inorganic particles and coatings. Additional coatings around the biopolymer matrix particles were applied using a spray coater. The system can be seen as a Trojan horse when anti-microbial compounds are entrapped. The particle stays dormant until initial microbial growth occurs. The microbe will recognise the particle as a source of food due to the biopolymers of which it consists. Prior to consumptions the microbe will start to excrete the proper enzymes to hydrolyse the biopolymers. The integrity of the particle is violated once the biopolymers starts to hydrolyse. Subsequently, the anti-microbial ingredients is secreted eliminating the microbe. The same principle can be applied to make anti-microbial coatings. Combined knowledge of biopolymers, micro-encapsulation techniques and the various applications allowed this development.

**EXPERTISE GROUP: THIN FILM TECHNOLOGY (TFT)**

TFT aims at deposition, protection and packaging solutions for innovative products to either capture or emit light, such as solar cells and light emitting diodes (LEDs). State-of-the-art technology for the production of multi-layer devices and materials and expertise in gas phase deposition, wet chemistry and multi-layer deposition is available.

**SPATIAL ATOMIC LAYER DEPOSITION**

There is an increasing interest in using polymer materials (foils and/or woven/ nonwoven fiber-based systems) as carriers for flexible applications. For example flexible displays, lighting, solar cells and sensors, but also food- and medical packaging. Surface functionalisation is often required to make the polymer surfaces suitable for a particular applications. One can think of increased barrier properties for oxygen and water for encapsulation, protection and packaging applications. Spatial atomic layer deposition (S-ALD) is a relevant technique that can be used to deposit thin (nm-μm) functional films on polymer surfaces. This is a technique developed by TNO and it combines the unique assets of ALD (unparalleled uniformity, conformality, thickness control and virtually pinhole free films) with industrially relevant deposition and throughput rates under atmospheric pressure. Examples of functional films that can be deposited are barriers and encapsulation for e.g. OLEDs, transparent conductors for solar cells and dielectric films for electronics.
MOLECULAR LAYER DEPOSITION

Molecular Layer Deposition (MLD) is a technique to deposit thin films of organic compounds and polymer materials. The technique is very similar to atomic layer deposition (used for inorganic materials), but it differs in the type of precursor. By using volatile organic precursors, thin and uniform organic films can be deposited from the gas phase on a wide range of substrates, where the nature of the film is determined by the precursor chemistry (i.e. hydrophobic, hydrophilic, dielectric, (semi)conducting, stress relief, etc.). The combination of MLD of organic films with ALD of inorganic films gives an even wider range of functionalities by combining the properties of the individual materials, for instance for making very thin and flexible ultrabarriers. Examples of functional films that can be deposited are barriers and encapsulation for e.g. OLEDs, transparent conductors for solar cells and dielectric films for electronics.

PLASMA PROCESSING

TFT has extensive knowledge and experience in low-temperature (20-60°C) and atmospheric-pressure plasma processing, which is a versatile technique that is increasingly used in surface and interface engineering.

A thin surface layer (±5 nm) is modified by this dry, cost-effective, and environmentally friendly technique; and the desired surface properties of various materials are achieved without altering the bulk material characteristics. Plasma treatment allows the achievement of a higher quality of surface characteristics than would otherwise be possible, as well as functionalisation of materials that are beyond the reach of traditional wet chemistry processing.

Low-temperature plasma processing can be classified into the following variations:
- Etching/cleaning, which involves the removal of material by the fragmentation of molecules on the treated surface.
- Surface activation, which uses mechanisms such as hydrogen abstraction, surface radical formation, and introduction of new functional groups from the plasma environment into the polymer chain being treated. Depending on the selected processing gas, a large variety of chemical groups can be incorporated into the surface like hydroxyl, carbonyl, amino and imino groups.
- Plasma-assisted grafting is a two-step process in which plasma activation is followed by exposure to a liquid or gaseous precursor, e.g., a monomer. The monomer then undergoes a conventional free radical polymerisation on the activated surface.
- Surface polymerisation introduces a monomer directly into a plasma, and the polymerisation occurs in the plasma itself.

Within TNO, we have been using mainly surface Dielectric Barrier Discharge (DBD) plasma sources in the form of flat-bed and jet for surface modifications of polymers, papers, metals, glass and ceramics in the form of (nano, micro) particles, filaments, yarns, woven and nonwovens, sheets, plates and foils. The following selected examples giving an indication of possible utilisation of plasma processing for smart materials’ processing:

SURFACE ACTIVATION

We have successfully demonstrated the activation of various materials, such as polyethylene, polypropylene, polyethyleneterephthalate, ETFE, PVDF, PTFE, but also paper, glass, some metals and TCO’s leading in dramatic increase of the surface energy.

POST-ACTIVATION PROCESSING

Such activation has been used to improve the application of coatings on surfaces by creating a similar molecular structure as the coating itself and hereby improve adhesion, improve the spreading of the coating material on the surface and hereby reduce the amount of applied coating, enhance the coating functionality.

As an example in the case of adhesion improvement of polyurethane and/or polyvinylchloride to PET, plasma activation could fully substitute for or outperform the current state-of-the-art adhesion-promoting treatment.

PLASMA-ASSISTED GRAFTING OF A BIOCIDES

TNO-synthesised quaternary-ammonium chemicals that have been successfully immobilised onto the surface of various plastics by means of plasma-assisted grafting. Plasma pre-treatment facilitated bonding of the antimicrobial chemicals to chosen substrates and resulted in enhanced antimicrobial performance. The advantage of this technique to induce antimicrobial properties, over e.g. the introduction of biocides, is that only the surface needs to be modified and the material does not leach.

Mechanism of antimicrobial action. The material has proven to be biocidal against a plurality of microbes, such as escherichia coli, staphylococcus aureus, pseudomonas earuginosa, streptococcus pyogenes A, E. faecalis etcetera.
PLASMA POLYMERISATION

Highly hydrophobic polymer layers were deposited for example on the cotton and aramid woven and nonwovens, and glass fibre nonwovens on the level of individual fibres by means of the plasma polymerisation of hexamethyldisiloxane (HMDSO). Hydrophilic plasma polymerised polyacrylic acid (PAA) coating have been deposited on PET and PP fabrics as well.

Water droplets on a HMDSO plasma treated cotton textile. The fabric is hydrophobically modified as is demonstrated by the droplets. Without the modification the water is absorbed in the fabric.

Plasma-polymer coatings containing agglomerated or well dispersed nanoparticles (e.g. TiO₂, ZnO, MgO) were successfully deposited on various textiles on the level of individual fibres. Nanomaterial was admixed to a precursor and agglomerated by an ultrasound processor. This technique has the potential to deposit nanocomposites on a variety of materials without any limitation on the type or concentration of nanomaterial.

Incorporation of TiO₂ nanoparticles in a plasma-polymer coating on fibres.

PLASMA-ASSISTED SELF-ASSEMBLY

We have demonstrated that plasma activation is a useful surface pre-treatment tool for self-assembly of polyelectrolytes, dyes and nanoparticles on a variety of substrates. Moreover, it indicated that e.g. ink-jet printing of polyelectrolyte of a high concentration and nanoparticles (e.g., in a paste form) might be a suitable alternative to traditional wet dip-coating using diluted polyelectrolytes, allowing high-precision deposition and dramatically reducing fabrication time and cost. Traditionally, the electrostatic layer-by-layer assembly technique requires long deposition times – usually around 10-15 minutes per a layer of a diluted electrolyte, at least 5 minutes rinsing and then 10-15 min of per a layer of an oppositely charged diluted electrolyte and once more again rinsing – this gives 1 bilayer. Normally, 15-100 bilayers are needed to achieve the desired properties. We showed that it is possible to use undiluted electrolytes and only 2-4 bilayers are enough to provide a coating of the same thickness in comparison with the conventional way. The traditional washing steps could be avoided. It is only required to put the final coating in an aqueous environment to allow intermixing of the applied electrolytes.

SEM micrographs of polyallylamine hydrochloride (PAH)/PAA coating (top) and MgO nanoparticles (bottom) deposited on a PET substrate.

EXPERTISE GROUP: STRUCTURAL RELIABILITY

Engineering of building materials, structural safety assessment, uncertainty analysis through probabilistic methods, service life prediction of materials and structures and evidence based design.

CEMENT-BASED BUILDING MATERIALS (CONCRETE, GEOPOLYMERS AND MASONRY)

IMPROVED CEMENT FOR ZONAL ISOLATION USING DEDICATED POLYMERS

Zonal isolation is required for the integrity of the bore hole in oil and gas recovery. A lot of well bores show failure of zonal isolation and this poses severe environmental and health risks since hydrocarbons or previously injected fluids leak to the surface or into nearby aquifers. A cement sheath is placed around the wellbore to provide zonal isolation. Cementing often results in defects in the formed cement sheath. TNO has developed an improved cement that uses dedicated polymers. This ultimately results in a cement-polymer composite sheath having less defects. Care must be taken with the selection of the polymers. Important aspects are: compatibility with cement mixture and cement setting chemistry, long time temperature stability and processability. In summary, this topic requires profound knowledge of enhanced oil and gas recovery, building materials and polymer chemistry and physics. Specialists from SR provide the cement chemistry knowledge, while specialists from R&M provide the polymer science, thus creating a new truly composite material.

Improved cement for zonal isolation in oil and gas recovery.

Shell Bi-lateral collaboration
UPGRADING WASTE STREAMS LIKE BOTTOM ASH TO NEW BUILDING MATERIALS
Concrete is the number one building material in the world. It consists of cement, sand, gravel and water: all primary materials dug up from our earth. TNO specialists from SR have realised that a majority of these materials can be replaced by secondary waste stream materials. Especially the use of cement, responsible for 5% of the man-made CO₂ production in the world, can be greatly reduced. SR specialists have the cement chemistry knowledge to activate inorganic aluminosilicate materials and produce binding materials from secondary resources like bottom ash from municipal waste incinerators. For ordinary Portland cement the main components consists of calcium-silica-oxides which react with water to form a calcium-silica-hydrate matrix structure. Bottom-ash with a high amount of amorphous silica oxides can be activated to form aluminosilicates (geopolymers). Similar knowledge can also be used to produce brick like material from construction and demolition waste streams. This would mean making stone-like material without going through an energy intensive high temperature oven process.

EU Sus-Con

BITUMINOUS ROAD MATERIALS
IMPROVING THE DURABILITY OF BITUMINOUS ROAD MATERIALS BY ADDING FIBER SYSTEMS
TNO has investigated the effect of short fiber addition to porous asphalt wearing courses in order to prolong service life of highway pavements. Critical conditions and loads were evaluated for fiber containing mixes versus reference mixes. Currently TNO works on the evaluation of the field performance of such fiber containing wearing courses in order to validate laboratory conclusions and give direction for optimisation of the fiber-asphalt composition for better field performance. Fibers could first prevent fatigue cracks to propagate through the material under continuous loading and second could help is distributing stresses as and effect of thermal expansion/shrinkage. The use of fibers in asphalt is not new, but normally fibers are only employed as a viscosity modifier and not for mechanical improvement. Hence instead of standard low-end cellulose fibers now high-end polyacrylonitrile fibers are used. In order to investigate their performances different sizes (lengths) of the fibers and concentration levels in the asphalt are evaluated. This topic requires expertise in civil engineering, polymer fiber (composite) mechanics and (polymer/bitumen) materials science.

PANACEA Co-financed collaboration
Lambda Furtherance BV
KWS Infra BV

REPLACING BITUMINOUS ROAD MATERIALS BY LIGNINE-BASED MATERIALS
In order to develop a more sustainable asphalt binder TNO has investigated the possibility to replace bitumen with bio-based material such as lignin derivatives. Together with expertise from Zeist on lignin materials bitumen specialists in SR have investigated the compatibility and stability of several lignin derivatives in bitumen in order to obtain analogue performance as regular asphalt binders. Currently the new, more sustainable, compositions are optimised and reformulated for optimal performance in asphalt mixes. Optimisation takes place by tailoring the mixing conditions (levels of shear, temperature etc) and type of lignin derivatives, as well as the level of addition. Because of the fact that current results are being reviewed for patent filing, no more specific info can be given. This topic requires expertise in civil engineering, organic (bio)chemistry and (polymer/bitumen) materials science.

ICOPAAL Co-financed collaboration
Van Gelder aanmenerij

IMPROVEMENT OF (SELF-)HEALING PROPERTIES IN ROAD CONSTRUCTION MATERIALS
Asphalt is known for its intrinsic (self) healing behaviour. Bitumen, a visco-elastic fluid binds the aggregate particles inside pavements and is able to reestablish bonding after fracture (at elevated temperatures). The process of healing of asphalt is poorly understood and it is unclear which constituents or which circumstances control/dominates the healing behaviour. The healing behaviour however has a significant impact on the fatigue resistance and controls in a large extent the design rules for a pavement. Understanding the healing behaviour and knowing how to optimise the mix in order to get better fatigue resistance will result in improved/innovative more-cost effective pavement constructions. Since the complexity of the healing phenomena is high a 4 year PhD position (2013-2017) for a TNO employee (G. Leegwater) on this topic was created at the TU Delft. The position is established within the collaboration between TU Delft, Rijkswaterstaat and TNO (i.e. Infraquest). This topic requires expertise in civil engineering and (polymer/bitumen) materials science.

IQ – PhD healing asfalt

Understanding intrinsic healing behaviour of asphalt.
EXPERTISE GROUP: MATERIALS FOR INTEGRATED PRODUCTS

The research group Materials for Integrated Products works on the design/modelling and assessment of micro- and nano-structured composite materials for extreme environments (very high or low temperatures, high pressures/forces, vacuum, radiation and chemicals).

MULTI-SCALE MODELLING APPROACHES

Computational modelling techniques are now widely employed in materials science, due to recent advances in computing power and simulation methodologies, since they can enable rapid testing of theoretical predictions or understanding of complex experimental data at relatively low cost. However, many problems at the leading edge of materials science involve collective phenomena that occur over a range of time and length scales which are intrinsically difficult to capture in a single simulation.

Within the group of Materials for Integrated Product (MIP) multiscale approaches are applied within a wide range of projects. Within ETP projects, the application of multiscale methods is mainly focused on simulations of material microstructure and mechanical properties.

For the ETP-FaiMoS, computational homogenisation of solid-fuel for the propulsion of rockets and sequential coarse graining of visco-elastic properties for asphalts have been successfully applied. ETP CMS has resulted in the development of a predictive tool, which enables the description and analysis of Representative Volume Elements (RVEs). RVEs are at the heart of many multiscale modelling schemes for heterogeneous materials, like asphalt, steel, metal-matrix-composites, steels, and ceramics. The development of these types of materials can strongly benefit from a better understanding of the mechanical responses related to the microstructural scale. So far, mainly structural properties have been considered. Recently, also multi-physics approaches have been adopted within the analysis of multi-scale problems, for example thermo-mechanics, opto-thermo and electro-mechanics. Besides considering heterogeneous materials, interfaces and their related physics and properties are becoming of increasing interest. In the structural domain interfaces strongly govern the overall strength and toughness of a (micro) structure. Moreover, in the thermal, electrical and optical domain interface properties can be tailored to exhibit desired overall properties and functionality.

ETP-Computation Material Science (CMS)

ETP-Failure Modules for Large Structures (FaiMoS)

ETP-Nanostructures

STRUCTURAL TOPOLOGY OPTIMISATION (ETP CMS)

In the near future, TNO aims to optimise material properties of multi-material systems. At this moment, it is possible to provide a stiffness difference in different directions for a certain object. Topology optimisation can then be applied to determine a free-form material-void structure with these different stiffnesses in the different directions. TNO aims for topology optimisation solutions where the user provides an anisotropic matrix of a certain material property and the simulation routine provides the multi-material structure resembling those properties.

ELECTRONIC MATERIALS

FLAKE/PARTICLE FILLED ADHESIVES FOR ELECTRONIC APPLICATIONS

In the bilateral project STACKiT particle-filled glues (with particles in the micrometre size), better known as anisotropic conductive films (ACFs), have been investigated. These ACFs are used to bond chips on glass in this specific case.

A software tool, based on both experimental work (inventory including QMAP (Qualitative Model for Analysis of a Production system),
material characterisation and failure analysis) and physical models (mainly through finite element analysis), was developed and built. This software tool indicates if the selected bonding parameters are in the correct regime (time, temperature and pressure).

In the ENIAC project SE2A TNO investigated the possibility of replacing traditional tin based solder joints with isotropic conductive adhesives with nanoparticles, called electrically conductive adhesives (ECA), for new generation automotive sensors. This research focused on experimental evaluation of ECA aging under accelerated stress conditions, relevant to automotive field conditions and a numerical study on residual stresses in the ECAs that occur during joining.

MOLDING COMPOUNDS FOR AUTOMOTIVE ELECTRONICS

Within the ENIAC SE2A project two topics in the field of moulding compounds for automotive electronics (packaging of for example ICs) were investigated: moisture modelling and die-moulding compound delamination.

**Moisture modelling**

A model was created which is able to predict the thermal and hygroscopic stresses (behaviour) within an electronic device. Such thermo-hygro-mechanical model of the moulding compound allows for prospective determination of stresses, during certain tests or during service life, caused by certain design changes of the product.

**Die-moulding compound delamination**

The main goals for this investigation was to determine the mechanism of delamination in silicon on insulators (SOI) package and to investigate ways to decrease the risk of delamination and secondly to determine the influence of polydimethylsiloxane (PDMS) contamination on delamination and to determine cleaning guidelines (i.e. max area contaminant).

**PIEZO-ELECTRIC MATERIAL BINDERS FOR SMART PRODUCT MANUFACTURING**

For decades, TNO has developed suitable binders and de-binder-processes for the sintering of various ceramics (alumina, silicon nitride, sialon, aluminum oxynitride (alon) and various titanates). Various agencies and recipes for adapted rheological properties of the binder/ceramic solutions were investigated. In addition to rules of thumb, in-depth analyses of particularly piezo-electric smart materials binder systems were analysed and developed. Recently focus was on ‘piezo-electric ceramic/polymer composites’, e.g. surfaces with switchable friction coefficient are demonstrated, see the figure below (D. van den Ende, APL 102(2013) 141603).

**TOPOLOGY OPTIMISATION FOR THERMAL AND ELECTRICAL DOMAIN**

TNO is working on topology optimisation for optimisation of the thermal and electrical properties of materials used in for example organic light emitting diodes (OLEDs) and solar cells. This work is mainly focused on the metal enhancements (grids) of the transparent electrodes in OLEDs and solar cells. Hence, instead
of pre-fixed grids patterns like H-grids, the optimisation procedure determines a freeform grid pattern which will result in the best homogeneity (OLED) or the highest power output (solar cell).

These simulations can also be performed in a multiphysics fashion, which is interesting in the case of OLEDs (electro-thermal optimisation). These freeform grid patterns are especially interesting in case of custom-sized/freeform OLED or solar cell shapes. As there is an analogy between the physical equations for electrical, thermal and moisture diffusion problems, all these problems can be solved with a similar modelling procedure. This method is also not limited to the described application; any kind of problem, where you want to minimise electrical resistance or maximise cooling, can be addressed (e.g. cooling channel geometry for liquid coolant).

**Application:**
- Holst
- Solar concentrator (CPV4all (FP7-ENERGY))
- FP7 EU-RU IM3OLED

**OPTIMISATION OF ANTI-REFLECTIVE COATINGS (ETP NANOSTRUCTURES)**
This project focuses on the application of (virtual) optimisation procedures for the design and production of novel anti-reflective coatings.
The two means of optimisation are:

1. Geometrical optimisation of thin layer structure (e.g. motheye) with respect to the optical properties (>99% absorption).

   **Application:**
   - Holst
   - Soliance
   - FP7 EU-RU IM3OLED

2. Process optimisation of nano-imprint procedure with respect to the manufacturability (low applied force, low T, high speed etc.).

**LIGHT MANAGEMENT**

**MATERIAL SOLUTIONS FOR OLEDs**

TNO works on two areas concerning light management: homogeneity and in/outcoupling structures. Electrical and electro-thermal simulations are applied to simulate/determine the homogeneity of OLEDs. Separate from that, 2D or 3D ray tracing (refraction and reflection) can be performed on structures with scattering particles or on structured in- or outcoupling layers (e.g. microspheres). These simulations can be used to optimise scattering particle densities and properties and microstructure geometry.
SENSOR INTEGRATION DESIGN
TNO is developing a method to integrate low cost optical sensors into a LED luminaire to detect daylight enabling energy (cost) saving. The challenges to integrate low cost sensors into the LED Luminaire are multiple: 1) High temperature changes can occur in the LED luminaire due to use in both indoor- and outdoor application ranging from −40 to +110°C; 2) The flux (light level) dynamic range that the sensors must cover are enormously ranging from a few Lux to more than 100 kLux; 3) The LED's are switched on/off with a high frequency (Hz) and current (A) leading to changing electrical fields. Those influences are influencing the sensor performance and is decisive for the to be used materials for the design and the integration into the LED luminaire.

Integral approach is needed to realise high precision optical sensors with low cost materials. Steady state and transient modelling has been done to create a sensitivity mapping of the most critical influences within a LED Luminaire. Thermal-, optical- and electrical experiments have been executed to verify the models and to create design guidelines for improved sensor performance using low cost materials. Here below an example of a steady state thermal simulation of a LED engine used in a LED luminaire with a daylight sensor integrated close to the LED’s.

EnLight

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