Chemically extracted nanocellulose from sisal fibres by a simple and industrially relevant process

A novel type of acetylated cellulose nanofibre (CNF) was extracted successfully from sisal fibres using chemical methods. Initially, a strong alkali treatment was used to swell the fibres, followed by a bleaching step to remove the residual lignin and finally an acetylation step to reduce the impact of the intermolecular hydrogen bonds in the nanocellulose. The result of this sequence of up-scalable chemical treatments was a pulp consisting mainly of micro-sized fibres, which allowed simpler handling through filtration and purification steps and permitted the isolation of an intermediate product with a high solids content. An aqueous dispersion of CNF could be obtained directly from this intermediate pulp by simple magnetic stirring. As a proof of concept, the dispersion was used directly for preparing a highly translucent CNF film, illustrating that there are no large aggregates in the prepared CNF dispersion. Finally, CNF films with alkali extracts were also prepared, resulting in flatter films with an increased mass yield and improved mechanical strength.
Development of a thiol-ene based screening platform for enzyme immobilization demonstrated using horseradish peroxidase

Efficient immobilization of enzymes on support surfaces requires an exact match between the surface chemistry and the specific enzyme. A successful match would normally be identified through time consuming screening of conventional resins in multiple experiments testing individual immobilization strategies. In this study we present a versatile strategy that largely expands the number of possible surface functionalities for enzyme immobilization in a single, generic platform. The combination of many individual surface chemistries and thus immobilization methods in one modular system permits faster and more efficient screening, which we believe will result in a higher chance of discovery of optimal surface/enzyme interactions. The proposed system consists of a thiol-functional microplate prepared through fast photochemical curing of an off-stoichiometric thiol-ene (OSTE) mixture. Surface functionalization by thiol-ene chemistry (TEC) resulted in the formation of a functional monolayer in each well, whereas, polymer surface grafts were introduced through surface chain transfer free radical polymerization (SCT-FRP). Enzyme immobilization on the modified surfaces was evaluated by using a rhodamine labeled horseradish peroxidase (Rho-HRP) as a model enzyme, and the amount of immobilized enzyme was qualitatively assessed by fluorescence intensity (FI) measurements. Subsequently, Rho-HRP activity was measured directly on the surface. The broad range of utilized surface chemistries permits direct correlation of enzymatic activity to the surface functionality and improves the determination of promising enzyme-surface candidates. The results underline the high potential of this system as a screening platform for synergistic immobilization of enzymes onto thiol-ene polymer surfaces. This article is protected by copyright. All rights reserved.
Shape optimization as a tool to design biocatalytic microreactors

Reactor design is commonly constrained to already well-known reactor shapes. This article presents an innovative application of shape optimization techniques to design biocatalytic microreactors. Currently, the optimization of reactor performance is often done by considering solely the process conditions. However, common reactor types used in (bio)chemical processes do not always give the optimal conditions for executing the
reaction, and it is therefore necessary to look into new approaches to further improve the performance of reactors. The new application of shape optimization described in this paper has as its main goal the design of a reactor by compensating for the limitations of the reaction system by modifying the reactor configuration. Random search was the optimization method chosen for transforming the initial reactor configuration to a more optimal one.

The case study presented here investigates the impact of a change to the microreactor shape on the active mixing of two parallel streams (one containing an enzyme, amino transaminase, and the other the substrates, acetophenone and isopropylamine) and consequently its influence on the reaction yield. Compared to the original reactor configuration, the shape optimization resulted in changes of the microreactor wall surfaces leading to an 8.4 fold improvement of the reactor yield. This innovative optimization also offers the opportunity to obtain new structures which can later be tested experimentally.

**General information**

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Organisations: Department of Chemical and Biochemical Engineering, CAPEC-PROCESS, The Danish Polymer Centre

Authors: Pereira Rosinha Grundtvig, I. (Intern), Daugaard, A. E. (Intern), Woodley, J. (Intern), Gernaey, K. (Intern), Krühne, U. (Intern)

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Soft and flexible conductive PDMS/MWCNT composites
Conductive elastomers based on MWCNT in polydimethylsiloxane (PDMS) have been prepared by a range of dispersion methods such as ultrasonication, speedmixing and roll milling in combination with physical or covalent modification. The ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, was used to pre-disperse MWCNT in a MWCNT/IL-gel that was used for preparation of MWCVNT/PDMS composites. The method was seen to be effective at low levels of MWCNT, but required combination with a roll mill to obtain a stable dispersion at 4 wt % MWCNT. With higher amounts of MWCNT a reduction in conductivity was observed, which was attributed to a change in morphology occurring between 4 and 5 wt % MWCNT. As an alternative to IL dispersing aids a novel functionalized MWCNT was prepared by free radical polymerization using α-methacryloxypropyl-polydimethylsiloxane, which could be used directly for preparation of MWCNT/PDMS composites. Composites prepared by use of the IL dispersion method, use of a roll mill or by use of the f-MWCNT all had conductivities around 0.005–0.01 s/cm and retained conductivity upon extension.

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Authors: Hassouneh, S. S. (Intern), Yu, L. (Intern), Skov, A. L. (Intern), Daugaard, A. E. (Intern)
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BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.658 SNIP 1.081 CiteScore 1.57
ISI indexed (2012): ISI indexed yes
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BFI (2011): BFI-level 1
Scopus rating (2011): SJR 0.601 SNIP 0.965 CiteScore 1.45
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BFI (2010): BFI-level 1
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Synthesis of a novel polyester building block from pentoses by tin-containing silicates

We report here the direct formation of the new chemical product, trans-2,5-dihydroxy-3-pentenoic acid methyl ester, from pentoses using tin-containing silicates as catalysts. The product is formed under alkali-free conditions in methanol at temperatures in the range 140–180 °C. The highest yields are found using Sn-Beta as the catalyst. Under optimised conditions, a yield of 33% is achieved. Purified trans-2,5-dihydroxy-3-pentenoic acid methyl ester was used for copolymerisation studies with ethyl 6-hydroxyhexanoate using Candida antarctica Lipase B as the catalyst. The copolymerisation yields a product containing functional groups originating from trans-2,5-dihydroxy-3-pentenoic acid methyl ester in the polyester backbone. The reactivity of the incorporated olefin and hydroxyl moieties was investigated using trifluoroacetic anhydride and thiol-ene chemistry, thus illustrating the potential for functionalising the new copolymers.

General information
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Organisations: Department of Chemistry, Organic Chemistry, Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Elliot, S. G. (Intern), Andersen, C. (Intern), Tolborg, S. (Intern), Meier, S. (Intern), Sadaba, I. (Ekstern), Daugaard, A. E. (Intern), Taarning, E. (Ekstern)
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Dielectric electroactive polymer comprising an elastomeric film in the form of a gel

Use of an elastomeric film in the form of a gel, wherein said gel is a non-conductive hydrogel or organogel, as a dielectric electroactive polymer.

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre  
Authors: Skov, A. L. (Intern), Daugaard, A. E. (Intern)  
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A comparison of partially acetylated nanocellulose, nanocrystalline cellulose, and nanoclay as fillers for high-performance polylactide nanocomposites

Partially acetylated cellulose nanofibers (CNF) were chemically extracted from sisal fibers and the performance of those CNF as nanofillers for polylactide (PLA) for food packaging applications was evaluated. Three PLA nanocomposites; PLA/CNF (cellulose nanofibers), PLA/CNC (nanocrystalline cellulose), and PLA/C30B (CloisiteTM 30B, an organically modified montmorillonite clay) were prepared and their properties were evaluated. It was found that CNF reinforced composites showed a larger decrease on oxygen transmission rate (OTR) than the clay-based composites; (PLA/CNF 1% nanocomposite showed a 63% of reduction at 238C and 50% RH while PLA/C30B 1% showed a 26% decrease) and similar behavior on terms of water vapor barrier properties with 46 and 43%, respectively of decrease on water vapor transmission rate at 238C and 50% RH (relative humidity). In terms of mechanical and thermomechanical properties,
CNF-based nanocomposites showed better performance than clay-based composites without affecting significantly the optical transparency.

**General information**
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, University of British Columbia, Université Grenoble Alpes
Authors: Trifol Guzman, J. (Intern), Plackett, D. (Ekstern), Sillard, C. (Ekstern), Hassager, O. (Intern), Daugaard, A. E. (Intern), Bras, J. (Ekstern), Szabo, P. (Intern)
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BFI (2012): BFI-level 1
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During recent years enzymatic polymerization has become increasingly popular as an alternative to classical polyesterification processes. The high regioselectivity observed for lipases permits preparation of novel polyesters with a high number of functional groups. This is particularly interesting when considering monomers from bio-based feedstock that generally contain a high number of functional groups such as both secondary and primary alcohols. Enzymatic polymerization can be conducted at relatively low temperature and thereby is well suited for sensitive monomers. Recently enzymatic polymerization was applied to prepare functional water soluble polyesters based on dimethyl itaconate and poly(ethyleneglycol). The monomer permits postfunctionalization using thiol-ene chemistry or aza-michael additions, which was used to illustrate the possibilities of preparing functional hydrogels. Hydrogels based on the polyesters were shown to be degradable and could be prepared either from the pure polyester or from prefunctionalized polyesters, though the thiol-ene reactions were found to be less effective. Since then a new monomer, trans-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM) has been prepared directly from pentoses using using tin containing zeolites. The monomer was prepared in yields of up to 32% and contains both a vinyl as well as a secondary alcohol in addition to the primary alcohol and ester functionality, and as such is an interesting building block for polymers. DPM was copolymerized together with ethyl-6-hydroxyhexanoate yielding copolymers with molecular weights of up to 12,000 g/mol. The polymers were postfunctionalized using trifluoroacetic anhydride, which resulted in 100% conversion of the secondary alcohols, illustrating the possibility to use the secondary alcohol for grafting. In addition to this, thiol-ene reactions using hexanethiol, mercaptoethanol, mercaptoacetic acid, 2-ethylhexanethiol and thiophenol were conducted on the internal double bond resulting in conversions of 32-100%. Given the lower reactivity of the internal double bond the extent of functionalization was found acceptable for use as a general method for dual functionality polyesters.
Hybrid nanocellulose/nanoclay composites for food packaging applications

In this research, cellulose nanofibres (CNFs) were extracted and dispersed through a combination of alkali-acetylation treatments followed by soft mechanical treatments. Thereafter, PLA-based nanocomposites with CNF, nanocrystalline cellulose (CNC) and/or commercially available nanoclay (Cloisite™ 30B) were prepared and evaluated for use in food packaging. It was determined that composites with CNF or CNC and clay led to a great reduction in the oxygen transmission rate (OTR) and the water vapour transmission rate (WVTR) (up to a 90% reduction in the OTR and 76% in the WVTR for PLA/CNF 5%/C30B 5%). A significant increase in thermomechanical resistance was obtained (the storage modulus of PLA/CNF 5%/C30B 5% at 85°C, was 3.7 times higher than for neat PLA) and increased crystallisation kinetics (the PLA/CNF 1%/C30B 1% showed an 81% reduction in half-crystallisation time compared with neat PLA) without a significant reduction in optical properties at moderate nanoparticle loading.

Furthermore, it was found that solvent casting at a low temperature induced sub-micron-sized spherulites, which had little influence on water diffusion and transparency decline. On the other hand, high temperature processing led to larger spherulite sizes, which had a more significant impact on water diffusion and transparency reduction but also showed an increased water sorption. Finally, it was found that cellulose nanofibers reduced water diffusion to an extent similar to C30B (21% vs. 27%), while hybrid composites showed 49% decrease, albeit CNF based composites showed increased water sorption (7% for PLA/CNF 1% composite and 9% for PLA/CNF 1%/C30B 1% when compared with neat PLA). The reduced diffusivity of the hybrid nanocomposites suggested that the material was promising for active packaging, since low diffusivity leads to the slower release of active compounds such as essential oils. On top of that the CNF was surface modified with hydrocinnamic acid (gCNF), with the aim of reducing even more the release rate of carvacrol and to enhance the CNF dispersion with the PLA matrix. Consequently, carvacrol-loaded PLA/CNF, PLA/gCNF and hybrid PLA/CNF/C30B composites were prepared and evaluated on controlled release applications. It was established that the surface modification of CNF greatly enhanced the dispersion of the gCNF and that carvacrol-loaded hybrid composites showed a decreased release rate, high ductility and a reduced WVTR which made those composites promising material for food packaging films.
Hybrid poly(lactic acid)/nanocellulose/nanoclay composites with synergistically enhanced barrier properties and improved thermomechanical resistance

Poly(lactic acid) (PLA)-based hybrid nanocomposites (PLA, nanoclay and nanocellulose) were prepared by reinforcing neat PLA with commercially available nanoclay (Cloisite C30B) and nanocellulose, in the form of either partially acetylated cellulose nanofibres (CNFs) or nanocrystalline cellulose. Composites with 1 or 5 wt% of nanocellulose, in combination with 1, 3 and 5 wt% of nanoclay, were prepared, and their barrier properties were investigated. It was found that the combination of clay and nanocellulose clearly resulted in synergistic behaviour in terms of the oxygen transmission rate (OTR) through a reduction of up to 90% in OTR and a further reduction in the water vapour transmission rate of up to 76%. In addition, the nanocomposite films showed improved thermomechanical resistance and improved crystallisation kinetics while maintaining high film transparency. This makes the hybrid PLA/CNF/C30B nanocomposites a very promising material for food packaging applications. © 2016 Society of Chemical Industry
Influence of surface modified nano silica on alkyd binder before and after accelerated weathering

Introduction of nano fillers in exterior wood coatings is not straightforward. Influence on aging of polymer binder needs to be taken into account along with possible benefits that nano fillers can provide immediately after application. This study shows the influence of two differently modified hydrophobic nano silica on an alkyd binder for exterior wood coatings. One month after application, the highest strength and energy required to break the films was obtained with addition of 3% disilazane modified silica. Changes in tensile properties were accompanied with a small increase in glass transition temperature. However, the highest stability upon accelerated weathering, measured by ATR-IR and DMA, was for nano composites with the highest amount of nano filler. The reasons for the observed changes are discussed together with the appearance of a feature that is possibly a secondary relaxation of alkyd polymer.

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The present study investigates the use of an open-air plasma-treatment system for the surface modification of polydimethylsiloxane (PDMS), in order to improve layer-to-layer adhesion. The procedure presented herein is more cost efficient compared to conventional vacuum-based plasma-treatment, and it is performed at different speeds and distances away from the nozzle, to investigate how these two parameters influence the resulting interfacial layer of two fully cured PDMS films. The plasma-treatment is determined not to alter mechanical properties compared to the single film, while peel forces are sufficient to avoid delamination during operation.

Monolithic PDMS Laminates for Dielectric Elastomer Transducers through Open-Air Plasma Treatment

The present study investigates the use of an open-air plasma-treatment system for the surface modification of polydimethylsiloxane (PDMS), in order to improve layer-to-layer adhesion. The procedure presented herein is more cost efficient compared to conventional vacuum-based plasma-treatment, and it is performed at different speeds and distances away from the nozzle, to investigate how these two parameters influence the resulting interfacial layer of two fully cured PDMS films. The plasma-treatment is determined not to alter mechanical properties compared to the single film, while peel forces are sufficient to avoid delamination during operation.

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Authors: Hassouneh, S. S. (Intern), Oubæk, J. (Ekstern), Daugaard, A. E. (Intern), Skov, A. L. (Intern)
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Polyhydroxyalkanoates (PHA) production from fermented crude glycerol by mixed microbial cultures.

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Authors: Burniol Figols, A. (Intern), Varrone, C. (Intern), Daugaard, A. E. (Intern), Skiadas, I. V. (Intern), Gavala, H. N. (Intern)
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Selective distribution of enzymes in a microfluidic reactor

Off stoichiometric thiol-ene mixtures are well suited for preparation of microfluidic devices with highly functional surfaces. Here a two stage process employing first thiol-ene chemistry (TEC) to prepare two opposite parts of a microfluidic system with a 30x30 mm reactor and subsequently a thiol-epoxy bonding was used to prepare a fully sealed microfluidic system. The reactor was surface functionalized in-situ with allyl glycidyl ether in different patterns (half-reactor, full-reactor, checkerboard structures) on the surface to provide a controlled distribution of epoxides. The method additionally enables the selective immobilization on either top-side or bottom-side or both sides of the reactor. Thereafter horseradish peroxidase was immobilized on the surface and activity tests illustrated how this distribution of the enzyme on the surface could be used to optimize the activity of the enzyme. The results were corroborated by CFD simulations.

The Current State of Silicone-Based Dielectric Elastomer Transducers

Silicone elastomers are promising materials for dielectric elastomer transducers (DETs) due to their superior properties such as high efficiency, reliability and fast response times. DETs consist of thin elastomer films sandwiched between compliant electrodes, and they constitute an interesting class of transducer due to their inherent lightweight and potentially large strains. For the field to progress towards industrial implementation, a leap in material development is required, specifically targeting longer lifetime and higher energy densities to provide more efficient transduction at lower driving voltages. In this review, the current state of silicone elastomers for DETs is summarised and critically discussed, including commercial elastomers, composites, polymer blends, grafted elastomers and complex network structures. For future developments in the field it is essential that all aspects of the elastomer are taken into account, namely dielectric losses, lifetime and the very often ignored polymer network integrity and stability.
Thiol-ene thermosets exploiting surface reactivity for layer-by-layer structures and control of penetration depth for selective surface reactivity.

Thiol-ene thermosets have been shown to be an efficient platform for preparation of functional polymer surfaces. Especially the effectiveness and versatility of the system has enabled a large variety of network properties to be obtained in a simple and straightforward way. Due to its selectivity, various thiols and allyl or other vinyl reactants can be used to obtain either soft and flexible or more rigid functional thermosets. The methodology permits use of either thermal or photochemical conditions both for matrix preparation as well as for surface functionalization. Due to excess reactive groups in the surface of thiol-ene thermosets, it is possible to prepare surface functional thermosets or to exploit the reactive groups for modular construction and subsequent chemical bonding. Here a different approach preparing monolithic layer-by-layer structures with controlled mechanical properties across freestanding samples is presented. The approach is further exploited for preparation of surface structures down to features of 25 µm scale by use of an absorber and simple masking. The combination of masking and absorbers were similarly used to prepare a reactor with controlled surface properties as shown in Figure 1. Here fully sealed reactors (Figure 1a) were prepared modularly by a combination of thiol-ene and thiol-epoxy curing reactions. The reactors were functionalized in different patterns on the top side of the assembled reactor, illustrating the effectiveness of absorbers in controlling the penetration depth and surface grafting. The methodology was used for surface immobilization of enzymes providing a direct link between the distribution of enzymes on the surface and the activity of the reactor.
Silicone chain extender
The present invention relates to a silicone chain extender, more particularly a chain extender for silicone polymers and copolymers, to a chain extended silicone polymer or copolymer and to a functionalized chain extended silicone polymer or copolymer, to a method for the preparation thereof and the use thereof.

A new soft dielectric silicone elastomer matrix with high mechanical integrity and low losses
Though dielectric elastomers (DEs) have many favourable properties, the issue of high driving voltages limits the commercial viability of the technology. Driving voltage can be lowered by decreasing the Young's modulus and increasing the dielectric permittivity of silicone elastomers. A decrease in Young's modulus, however, is often accompanied by the loss of mechanical stability and thereby the lifetime of the DE. A new soft elastomer matrix, with no loss of mechanical stability and high dielectric permittivity, was prepared through the use of alkyl chloride-functional siloxane copolymers. Furthermore, the increase in dielectric permittivity (43%) was obtained without compromising other important properties of DEs such as viscous and dielectric losses as well as electrical breakdown strength.
Aza-Michael addition reaction: Post-polymerization modification and preparation of PEI/PEG-based polyester hydrogels from enzymatically synthesized reactive polymers

The utility of aza-Michael addition chemistry for post-polymerization functionalization of enzymatically prepared polyesters is established. For this, itaconate ester and oligoethylene glycol are selected as monomers. A Candida Antarctica lipase B catalyzed polycondensation reaction between the two monomers provides the polyesters, which carry an activated carbon-carbon double bond in the polymer backbone. These electron deficient alkenes represent suitable aza-Michael acceptors and can be engaged in a nucleophilic addition reaction with small molecular mono-amines (aza-Michael donors) to yield functionalized linear polyesters. Employing a poly-amine as the aza-Michael donor, on the other hand, results in the formation of hydrophilic polymer networks.
Bio-based alkyds by direct enzymatic bulk polymerization

Alkyd coating systems have been largely used to preserve exterior wood applications as well as to provide them with a decorative appearance. In the current stage of sustainability concerns, there has been a stronger focus on development and production of bio-based coating components, heading toward a totally bio-based formulation. In this context, the biggest challenge is development of bio-based analogues to classical alkyd resins (or alkyd), which is up to 50% fossil based. In addition, all the remaining components of an alkyd coating formulation are also needed to be prepared from renewable raw materials before a 100% bio-based alkyd paint can be realized.

In this project an enzyme catalyzed bulk polymerization method for direct production of alkyds has been developed. The objective has been to make it possible to produce binders at much lower temperatures as well as to achieve a higher degree of control over the polymerization reaction. The process was used to prepare new and 100% bio-based resins. The developed enzymatic method is simple to perform, robust and allows the preparation of alkyds with much higher control
over the chemical structure compared with the corresponding traditional method. Bio-based alkyds prepared from a combination of glycerol, and tall oil fatty acids, and azelaic acid by enzymatic polymerization show improved hydrophobicity and lower glass transition temperatures compared to an alkyd prepared from the same raw materials by a classical boiling method. The enzymatic method results in a higher degree of control over the polymerization process, making it possible to optimize the binder structure to a specific degree of branching. Alkyd photostability of glycerol-based alkyds can be improved by increasing the alkyd’s branching level, and subsequent development resulted in optimized structures. It was aimed for further improvement of alkyd photostability through the development of new pentaerythritol-incorporated alkyds with high degree of branching. In order to make it possible to incorporate pentaerythritol into alkyd structures in enzymatic polymerization, a new type of pentaerythritol derivatized with azelaic acid (or penta-aze) was examined and tested for the production of more branched alkyd systems. A photostability test validated the concept, and the method also resulted in alkyds with improved hydrophobicity and lower glass transition temperatures compared to a corresponding classical reference. In a further development of the system, it has been found possible to use the esters of pentaerythritol and stearic acid in combination with the penta-aze derivative for the preparation of pseudo alkyds containing only pentaerythritol as polyol with high degree of branching. Moreover, the studies on more sensitive monomers such as itaconic acid in enzymatic polymerization has showed that the method is useful in the production of alkyds from such building blocks, which could not be prepared by the corresponding classical boiling method at high temperature. Such systems are considered as a good option for binders with improved curing properties.

In the project various aspects of preparing a bio-based alkyd formulation have also been investigated. In particular, a reaction setup for production of larger amounts of traditional alkyds was designed to allow the production of up to 500 grams of alkyds under inert atmosphere. This system has been used for preparation of a number of bio-based alkyds by classical cooking and provided a selection of physical properties as a function of diacid chain length. The synthesis set up was developed further to enhance reproducibility and emulsification of binders, which ultimately resulted in production of 300 g of a fully biobased alkyd. This binder was efficiently emulsified with a bio-based emulsifier, formulated and subsequently sent to an outdoor exposure, where it will be evaluated over the coming years.

Finally, the project has also been working on the coupling between reinforcement agents and the binder in alkyd coatings. For this purpose, two different types of silica particles were modified with rape seed oil fatty acids or tall oil fatty acids (TOFA-silica), respectively. Tests of TOFA-silica particles have demonstrated that their functionalized surface markedly altered their solubility, but provided only moderate improvement in the mechanical properties of the alkyd.

The development of elastomer materials with a high dielectric permittivity has attracted increased interest over the past years due to their use in, for example, dielectric elastomers. For this particular use, both the electrically insulating properties - as well as the mechanical properties of the elastomer - have to be tightly controlled in order not to destroy favorable elastic properties by the addition of particles. This study focuses on improving the electromechanical properties of an enhanced PDMS matrix with expanded graphite (EG) as filler. The PDMS matrix is crosslinked by means of an 8-functional crosslinker, which allows for development of a suitable network matrix. The dielectric permittivity was increased by almost a factor of 4 compared to a benchmark silicone elastomer.
Dielectric properties of ultraviolet cured poly(dimethyl siloxane) sub-percolative composites containing percolative amounts of multi-walled carbon nanotubes

In this study a new method of multi-walled carbon nanotube (MWCNT) incorporation was employed in the preparation of ultraviolet (UV) curable MWCNT-filled poly(dimethyl siloxane) (PDMS) composites. The composites were designed to
contain amounts of MWCNT above the percolation threshold, without becoming conductive. Ultrasonicated and dispersed MWCNTs were co-precipitated together with an excess of short chain alpha, omega-vinyl terminated PDMS with a deficient amount of thiol-crosslinker and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) into MeOH. The entire mixture was UV irradiated, resulting in a layer of hyperbranched PDMS forming around the MWCNTs. This MWCNT mixture was added to a hyperbranched long chain PDMS to provide concentrations of MWCNT of 0.33%, 0.66% and 1%, and a fully crosslinked system was obtained in a final photochemical curing. Rheology of the composites showed a moderate decrease in storage modulus (G') across the entire frequency range in line with an increasing amount of MWCNT, thus demonstrating that the rheological percolation threshold was not reached throughout the concentration range. Dielectric spectroscopy measurements showed an increase in permittivity in line with an increasing MWCNT content as well as the desired frequency-dependent conductivity for all samples. The composites showed moderate dielectric breakdown strength of 48 V μm(-1) at 0.33 wt% MWCNT, which decreased throughout the samples to 20 V μm(-1) at 1 wt%. Temperature-dependent AC conductivity studies revealed that an increase in the sample temperature could explain the premature breakdown observed for those composites with higher MWCNT loading.

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**Enzymatic polymerization of bio-based monomers for applications in hydrogels and coatings**

Enzymatic polymerization has been gradually building up during the last 30 years as an alternative to classical polyesterification processes, which permits preparation of polyesters under more benign conditions with high selectivity1.
In particular, the high selectivity is an interesting property of the enzymatic catalysts that can provide control over polymer structure in functional polymers.

Lipase catalyzed polymerizations (specifically CALB) has been applied to prepare functional polyesters and to evaluate the possibilities of using less stable bio-based monomers such as itaconic acid or its derivatives. Through variation of starting materials, several different functional polyesters have been prepared with the purpose of exploiting the selectivity of the enzymes to prepare polyesters with a controlled degree of branching. Branched polyesters find application in coatings and some of the prepared systems will be discussed in relation to alkyl coatings.

By combination with longer chain water soluble polymers such as PEGs it is also possible to prepare water soluble polyesters with some control over the endgroup structure. In combination with different carboxylic acids, functional polyesters based on PEG have been prepared and functionalized through aza-michael additions as well as through thiol-ene chemistry. Thereby the enzymatically prepared polymer backbone can be considered a scaffold for functional water soluble materials. Finally, these polymers have been applied for preparation of hydrogels, aiming at the potential use of these materials in drug delivery.

**Functional silicone copolymers and elastomers with high dielectric permittivity**

Dielectric elastomers (DEs) are a new and promising transducer technology and are often referred to as ‘artificial muscles’, due to their ability to undergo large deformations when stimulated by electric fields. DEs consist of a soft and thin elastomeric film sandwiched between compliant electrodes, thereby forming a capacitor. Silicone elastomers are one of the most used materials for DEs due to their high efficiency, fast response times and low viscous losses. The major disadvantage of silicone elastomers is that they possess relatively low dielectric permittivity, which means that a high electrical field is necessary to operate the DE. The necessary electrical field can be lowered by creating silicone elastomers with higher dielectric permittivity, i.e. with a higher energy density. The aim of this work is to create new and improved silicone elastomers with high dielectric permittivity. This was done through the synthesis of new functionalizable silicone copolymers that allow for the attachment of high dielectric permittivity molecules through copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) reactions. The synthesised silicone copolymers were prepared via the tris(pentafluorophenyl)borane catalysed Piers-Rubinsztajn reaction and have a high degree of chemical freedom, as several parameters can be varied during the preparation phase. Thus, the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the high dielectric permittivity molecules. Furthermore, the degree of functionalization of the copolymers can be varied accurately by changing the feed of the high dielectric permittivity molecules. As a result, a completely tuneable elastomer system, with respect to functionalization, is achieved.

**Functional silicone elastomers via novel siloxane copolymers and chain extenders**

Functional silicone polymers and elastomers with altered/improved bulk and/or surface properties are highly desired to expand the application range even further. Novel functional silicone polymers and elastomers were prepared via two different methods. One method was through the synthesis of siloxane copolymers via the tris(pentafluorophenyl)borane catalysed Piers-Rubinsztajn reaction, which allows for the attachment of functional molecules through copper-catalysed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The synthesised copolymers allow for a high degree of chemical freedom, as several parameters can be varied during the preparation phase. As an example, the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the functional molecules. Furthermore, the degree of functionalisation of the copolymers can be varied accurately by changing the feed of functional
molecules. As a result, a completely tuneable elastomer system, with respect to functionalisation, is achieved. The second method of functionalising silicone elastomers involves the synthesis of a so-called 'chain extender' that allows for chemical modifications such as CuAAC. This route is promising as an easy-to-use additive to commercial RTV silicone elastomer systems. We have investigated how the different functionalisation variables affect elastomer properties including dielectric and viscoelastic properties.

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Nanocellulose fibers applied in PLA composites for food packaging applications
Poly (lactic acid) (PLA) has long been advocated as one of the best candidates for bio-based food packaging, but low thermal stability, slow crystallization, high oxygen and water permeability are drawbacks that still limits the use of PLA in a broader range of applications. The goal of this research project has been to improve the permeability of PLA by use of nanocellulose or by combination of nanocellulose and nanoclay in PLA composites. The cellulose nanofibers (CNF) were extracted from sisal fibers using an optimized up-scalable three-step chemical protocol. Composites with both CNF and nanoclay resulted in highly transparent films with good termomechanical properties. Furthermore, the combination of nanocellulose and nanoclay led to a faster crystallization (80% reduced half crystallization time). In addition, hybrid composites was identified as an effective way to improve the barrier properties of PLA. In particular 1 wt% of CNF and NC resulted in a 63% of reduction on the oxygen transmission rate and a 57% on the water vapor transmission rate, while a 5 wt% PLA/CNF/NC resulted in a 89% and a 75% of decrease respectively.

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Optimization of large-scale fabrication of dielectric elastomer transducers
Dielectric elastomers (DEs) have gained substantial ground in many different applications, such as wave energy harvesting, valves and loudspeakers. For DE technology to be commercially viable, it is necessary that any large-scale production operation is nondestructive, efficient and cheap. Danfoss PolyPower A/S employs a large-scale process for manufacturing DE films with one-sided corrugated surfaces. The DEs are manufactured by coating an elastomer mixture to a corrugated carrier web, thereby imprinting the corrugations onto the elastomer. The corrugated elastomer is then sputtered with metal electrodes on the corrugated surface, and due to these corrugated surfaces the metal electrodes maintain conductivities up to more than 100% strain of the elastomer film. The films are then laminated in multiple layers to fabricate DE transducers. However, the current manufacturing process is not trouble-free, and two issues in particular have great influence on the performance of DE transducers. The first issue is the release of the corrugated elastomer film from the carrier web, due to the large surface area and flexible nature of the elastomer film, while the second issue relates to the lamination of DE films. Currently, the films are contacted without adhesion, in order to yield double-sided corrugations, which in turn causes friction between the
Polydimethylsiloxane (PDMS) elastomers employing conductive fillers are used in many applications for e.g. flexible electrode materials or with lower amounts of fillers for high capacitance elastomers. Traditionally, the most used filler in these applications has been carbon black, which through high loading results in sufficiently high conductivities. During recent years, the range of conductive fillers has been extended to include i.e. expanded graphite, single walled carbon nanotubes and multi walled carbon nanotubes (MWCNT), whereof in particular MWCNT are interesting due to their outstanding electrical and mechanical properties. However, the use of MWCNT for many new applications requires efficient processing strategies in order to result in elastomers with an efficient dispersion of the nanomaterial. If it is possible to obtain an efficient dispersion of the nanomaterial in the PDMS precursors the mixture should additionally be able to crosslink without interference from the nanofiller1. There are several possible pathways to obtain such dispersions, where these could be divided into two main strategies, direct mixing using processing equipment or modification of the MWCNT followed by traditional preparation of the crosslinked elastomer. Both pathways have been investigated and the presentation will outline results from both approaches.

Direct processing of the MWCNT together with PDMS prepolymer by mechanical mixing, sonication, speed mixing or roll milling has been investigated. It is very clear that in order to obtain sufficiently effective dispersion, it is necessary to use the more efficient methods such as roll milling or speed mixing to distribute the fillers. Processing aids such as ionic liquids have been tested and found effective, though it requires higher amounts of additive or combinations with the most effective mixing methods and a thorough mixing in order to provide good dispersions.
As an alternative to direct mixing, modification of MWCNT is a well-known approach to ease dispersion of nanomaterials. This can be done by surface initiated polymerizations by e.g. atom transfer radical polymerization (ATRP) using compatibilizing monomers. Through the surface initiated polymerization a thin coating of polymer is introduced on the MWCNT to prevent agglomeration and permit much easier dispersion into the targeted polymer such as a PDMS prepolymer. Through simple methods of either entrapment or free radical grafting methods functionalized MWCNT (f-MWCNT) are prepared and applied in preparation of elastomers resulting in easy and efficient dispersion of the nanofillers in the elastomer. In addition to this, the choice of method permits preparation of composites with either well distributed fillers or entrapped fillers providing access to high capacitance composites with an artificially high percolation threshold or to obtain conductive elastomers with a MWCNT loading of 5 wt% only.

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Technical University of Denmark
Authors: Hassonueh, S. S. (Ekstern), Goswami, K. (Intern), Skov, A. L. (Intern), Daugaard, A. E. (Intern)
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**Preparation and characterization of polyacrylamide-modified kaolinite containing poly [acrylic acid-co-methylene bisacrylamide] nanocomposite hydrogels**

Novel nanocomposite hydrogel structures based on cross-linked poly(acrylic acid) (PAA) and kaolinite (Kaol), modified with different loadings of polyacrylamide (PAAm), were prepared by inverse dispersion polymerization. Ceric ammonium nitrate as an initiator in the presence of nitric acid was used to graft PAAm from the Kaol surface. The surface-modified Kaol showed enhanced interactions between the filler and the PAA matrix, through interactions between amino (-NH2) from PAAm and carboxylic groups (-COOH) from PAA. The XRD and TEM measurements confirmed the exfoliated nanocomposites with the Kaol filler. The swelling degree (SD) of the swollen hydrogel nanocomposite was increased following the addition of polyacrylamide-modified Kaol particles into the hydrogel structures. Rheological characterization showed that an increase in the storage modulus (G’) could be a consequence of a good dispersion of Kaol particles in the polyacrylic acid matrix, thereby leading to enhanced interactions and furthermore to improved mechanical properties of the final hydrogels.

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Preparing mono-dispersed liquid core PDMS microcapsules from thiol–ene–epoxy-tailored flow-focusing microfluidic devices

An applied dual-cure system based on thiol–ene and thiol–epoxy “click chemistry” reactions was proved to be an extremely effective and easy to use tool for preparing microfluidic chips, thereby allowing for precise control over material properties and providing the possibility of covalently bonding chip wafers. Different thiol–ene–epoxy-based polymer compositions were tested with the help of DSC and ATR FTIR, in order to investigate their physical and chemical properties. Water contact angles were determined, thus verifying the high efficiency and selectivity of the chemical surface modification of compositions in relation to high hydrophilicity and hydrophobicity. An obtained microfluidic device was subsequently used in order to produce PDMS microcapsules of very narrow size distribution and which contained various common liquids, such as water and ethanol, as well as an ionic liquid 2-hydroxyethylammonium formate.
Silicone elastomers with high dielectric permittivity and high dielectric breakdown strength based on tunable functionalized copolymers

High driving voltages currently limit the commercial potential of dielectric elastomers (DEs). One method used to lower driving voltage is to increase dielectric permittivity of the elastomer. A novel silicone elastomer system with high dielectric permittivity was prepared through the synthesis of siloxane copolymers, thereby allowing for the attachment of high dielectric permittivity molecules through copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The synthesized copolymers allow for a high degree of chemical freedom, as several parameters can be varied during the preparation phase. Thus, the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the dipolar molecules. Furthermore, the degree of functionalization can be varied accurately by changing the feed of dipolar molecules. As a result, a completely tunable elastomer system, with respect to functionalization, is achieved. It is investigated how the different functionalization variables affect essential DE properties, including dielectric permittivity, dielectric loss, elastic modulus and dielectric breakdown strength, and the optimal degree of chemical functionalization, where these important properties are not significantly compromised, is also determined. Thus, the best overall properties were obtained for a silicone elastomer prepared with 5.6 wt% of the dipolar molecule 1-ethyl-4-nitrobenzene. Here, a high increase in dielectric permittivity (~70%) was obtained without compromising other vital DE properties such as elastic modulus, gel fraction, dielectric and viscous loss and electrical breakdown strength.

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Novel method to prepare multiwalled carbon nanotube/poly(dimethyl siloxane) (MWCNT/PDMS) non-conducting composites

In this study, a new method of carbon nanotube (CNT) incorporation was employed for the preparation of ultraviolet (UV) curable CNT filled poly (dimethyl siloxane) (PDMS) composites. The composites were designed to contain loadings of CNT above the percolation threshold without becoming conductive due to a localized distribution of CNT. Ultrasonicated and dispersed multiwalled CNTs were mixed with short chain vinyl terminated PDMS. When the whole mixture containing dispersed CNT and short chain PDMS was irradiated with UV radiation in the presence of a deficiency amount of hexafunctional thiol PDMS crosslinker and a photoinitiator, hyperbranched PDMS layers were formed over the CNTs. The prepared hyperbranched CNTs were mixed in different weight ratios (0.33%, 0.66%, 1%) with long chain vinyl terminated PDMS and crosslinked subsequently with the same hexafunctional thiol PDMS via UV photoinitiated thiol-ene chemistry to obtain the networks. Rheology of the prepared networks showed a gradual decrease in storage modulus (G') in the entire frequency range as the amount of CNT was increased due to a reduction in crosslinking density imposed by the CNT. Dielectric spectroscopy measurements showed an increasing trend in permittivity in all the composites with increasing CNT loadings and AC conductivity measurements confirmed non-percolating behavior of the prepared composites.

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Poly(lauryl acrylate) and poly(stearyl acrylate) grafted multiwalled carbon nanotubes for polypropylene composites

Two new polymer grafts on an industrial grade multiwalled carbon nanotube (MWCNT) were prepared through a non-oxidative pathway employing controlled free radical polymerization for surface-initiated polymer grafting. After photochemical introduction of an ATRP initiator onto the MWCNT, polymerizations of lauryl or stearyl acrylate were performed, resulting in two novel polymer modifications on the MWCNT (poly(lauryl acrylate) or poly(stearyl acrylate)). The method was found to give time dependent loading of polymers as a function of time (up to 38 wt% for both acrylates), and showed a plateau in loading after 12 h of polymerization. The modified nanomaterials were melt mixed into polypropylene composites with very low filler loading (0.3 wt%), whereafter both the thermal and electrical properties were investigated by DSC and dielectric resonance spectroscopy. The electrical properties were found to be substantially improved, where poly(lauryl acrylate) was found to be the superior surface modification, resulting in a conductive composite.
Silicone elastomers with high dielectric permittivity and high dielectric breakdown strength based on dipolar copolymers

Dielectric elastomers (DES) are a promising new transducer technology, but high driving voltages limit their current commercial potential. One method used to lower driving voltage is to increase dielectric permittivity of the elastomer. A novel silicone elastomer system with high dielectric permittivity was prepared through the synthesis of siloxane copolymers, thereby allowing for the attachment of high dielectric permittivity molecules through copper-catalysed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The copolymers have a high degree of chemical freedom, as the dimethylsiloxane spacer units between the functional groups, as well as the degree of functionalisation, can be varied. Thus, the best overall properties were obtained for an elastomer prepared with a copolymer with a 1200 g mol\(^{-1}\) dimethylsiloxane spacer unit and 5.6 wt% of the high dielectric permittivity molecule 1-ethynyl-4-nitrobenzene. Here, a high increase in dielectric permittivity (similar to 70%) was obtained without compromising other favourable DE properties such as elastic modulus, gel fraction, dielectric loss and electrical breakdown strength. © 2014 Elsevier Ltd. All rights reserved.
The objective of this thesis was preparation and characterizations of high permittivity ultraviolet (UV) cured elastomeric networks and composites applicable as dielectric electroactive polymers (DEAPs). At present, none of the commercially available elastomers such as acrylics, poly (dimethyl siloxane) (PDMS) and polyurethanes are designed with the requirements specific for DEAPs. Thus there is a need to develop elastomers with low elastic modulus, low viscous and dielectric losses and high relative permittivity. Interpenetrating networks and fumed silica reinforced composites of poly (propylene oxide) (PPO) were prepared which showed marked improvements in properties compared to the acrylic elastomers. But difficulties in curing by industrial processes and handling of these elastomers posed as limitations. So the focus was on optimizing UV induced thiol-ene reactions for curing commercially available PDMS. UV curing of PDMS was successfully established which eliminated the major drawbacks of widely used platinum catalyzed addition curing of PDMS. An advanced sequential curing used to form the PDMS networks showed low elastic modulus and low viscous losses than the former-developed processes due to better control over the heterogeneity of the networks. The sequential curing approach was successfully used to incorporate conductive multiwalled carbon nanotubes (MWCNTs) in higher concentrations than usual without making the elastomers conductive. The PDMS-MWCNT composites also showed high relative permittivity, low elastic modulus and low viscous and dielectric losses. Thus the elastomers developed in this project show promising properties to be considered as potential DEAPs.
Synthesis of telechelic vinyl/allyl functional siloxane copolymers with structural control

Multifunctional siloxane copolymers with terminal vinyl or allyl functional groups are synthesised through the borane-catalysed polycondensation of hydrosilanes and alkoxysilanes. Copolymers of varying molecular weights (\( M_w = 13200 - 70300 \) g mol\(^{-1}\)), spatially well-distributed functional groups and high end-group fidelity are obtained in a facile and robust synthetic scheme involving polycondensation, end-group transformation and different functionalisation reactions such as Cu(I)-mediated azide–alkyne cycloaddition. Pendant alkyl chloride, alkyl azide, bromoisobutyryl, 4-nitrobenzene and 1-ethyl-imidazolium chloride fragments with programmable spatial distributions are incorporated in the copolymer backbones. NMR and FTIR spectroscopy as well as size exclusion chromatography corroborate the efficacy and versatility of this modular approach.
Synthetic Strategies for High Dielectric Constant Silicone Elastomers

Dielectric electroactive polymers (DEAPs) are a new and promising transducer technology and are often referred to as 'artificial muscles', due to their ability to undergo large deformations when stimulated by electric fields. DEAPs consist of a soft and thin elastomeric film (an elastomer) sandwiched between compliant electrodes and have many interesting properties such as a simple working principle, large achievable strains, high-energy densities and the fact that they are lightweight and low in cost. Some issues, however, limit the current commercial viability of the technology, as high driving voltages (several kV's), for instance, are necessary to activate the material. Driving voltage can be lowered by increasing the energy density of the DEAP elastomer film, achieved by creating elastomers with high dielectric constants, which is a material's ability to store electrical energy. Two synthetic strategies were developed in this Ph.D. thesis, in order to create silicone elastomers with high dielectric constants and thereby higher energy densities. The work focused on maintaining important properties such as dielectric loss, electrical breakdown strength and elastic modulus. The methodology therefore involved chemically grafting high dielectric constant chemical groups onto the elastomer network, as this would potentially provide a stable elastomer system upon continued activation of the material. The first synthetic strategy involved the synthesis of a new type of cross-linker for silicone polymer networks. The silicone compatible cross-linker allowed for copper-catalysed azide-alkyne cycloadditions (CuAAC) and thereby the attachment of functional groups to the network crosslinking point. The functional groups were very well-distributed in the silicone elastomer matrix, and various functional groups provided a number of elastomers with diverse properties. High dielectric constant molecules, such as the dipolar 4-nitrobenzene and nitroazobenzene, resulted in elastomers with an approximately 20% increase in dielectric constant at low concentrations of dipolar species (~0.5 wt%). The second synthetic strategy was to create elastomers with high concentrations of functional groups and thereby even higher dielectric constants through the synthesis of novel copolymers. Two different routes were followed to accomplish this aim. One route involved the synthesis of a so-called 'chain extender' that allowed for chemical modifications such as Cu-AAC. This route was promising for one-pot elastomer preparation and as a high dielectric constant additive to commercial silicone systems. The second approach used the borane-catalysed Piers-Rubinsztajn reaction to form spatially well-distributed copolymers where functional groups could be attached along the polymer backbone. The functional copolymers contained vinyl or allyl end groups that allowed for elastomer synthesis. The dielectric properties of the formed elastomers were found to increase significantly and an optimum concentration of functional groups was identified. At a concentration of 5.6 wt% of a nitrobenzene functional group the dielectric permittivity increased 70% while at this loading important properties such as electrical breakdown strength, elastic modulus and dielectric loss were not significantly compromised. The developed synthetic strategies facilitate new ways of functionalising elastomers in general and dielectric elastomers in particular.

Tunable Surface Properties of a Conductive PEDOT/EVAL blend

Conductive polymers have been studied extensively during recent years. Especially, poly(3,4-ethylenedioxythiophene) (PEDOT) have found many application areas and are broadly considered one of the most promising conductive polymers. In order to broaden the application field of PEDOT we have developed an azide functional poly(3,4-ethylenedioxythiophene) (PEDOT-N3). The azide functional conductive polymer can be postpolymerization functionalized...
to introduce a large range of molecules onto the conductive backbone through click chemistry. Here we present a study of the incorporation of poly(ethylene-co-vinyl alcohol) (EVAL) into a copolymer of EDOT and EDOT-N$_3$ (poly(EDOT-co-EDOT-N$_3$)). Poly(ethylene-co-vinyl alcohol) (EVAL) is known to swell in polar solvents, which was exploited in this study to permit a good blending of the two polymers. Since both polymers have residual functional groups, the polymer blend permits post-functionalization through either the alcohols from EVAL or the azides from EDOT-N$_3$ (as shown in Scheme 1 below). In addition to this, the influence of the EVAL incorporation on the mechanical properties is tested. The presented procedure is a simple and easy way to prepare functional PEDOT(N$_3$) with a substantially improved mechanical stability. The increase in mechanical stability together with high functionality broadens the possible applications of PEDOT as a mechanically stable polymer.

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Authors: Pizzi, E. (Ekstern), Martinelli, A. (Ekstern), D'Ilario, L. (Ekstern), Hvilsted, S. (Intern), Daugaard, A. E. (Intern)
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UV-Cured, Platinum-Free, Soft Poly(dimethylsiloxane) Networks
To overcome the drawbacks exhibited by platinum-catalyzed curing of silicones, photoinitiated thiol–ene cross-linking of high-molecular-weight poly(dimethylsiloxane) (PDMS) prepolymers has been investigated as a pathway to novel soft PDMS networks, based on commercially available starting materials was developed. Through a fast and efficient two-step cross-linking reaction highly flexible PDMS elastomers were prepared.

General information
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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Goswami, K. (Intern), Skov, A. L. (Intern), Daugaard, A. E. (Intern)
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BFI (2014): BFI-level 2
Scopus rating (2014): SJR 2.487 SNIP 1.219 CiteScore 5.51
Web of Science (2014): Indexed yes
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Scopus rating (2013): SJR 2.604 SNIP 1.239 CiteScore 5.68
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Visualisation and characterisation of heterogeneous bimodal PDMS networks

The existence of short-chain domains in heterogeneous bimodal PDMS networks has been confirmed visually, for the first time, through confocal fluorescence microscopy. The networks were prepared using a controlled reaction scheme where short PDMS chains were reacted below the gelation point into hyperbranched structures using a fluorescent silicone compatible cross-linker. The formation of the hyperbranched structures was confirmed by FTIR, 1H-NMR and size exclusion chromatography (SEC). The short-chain hyperbranched structures were thereafter mixed with long-chain hyperbranched structures to form bimodal networks with short-chain domains within a long-chain network. The average sizes of the short-chain domains were found to vary from 2.1 to 5.7 mm depending on the short-chain content. The visualised network structure could be correlated thereafter to the elastic properties, which were determined by rheology. All heterogeneous bimodal networks displayed significantly lower moduli than mono-modal PDMS elastomers prepared from the long polymer chains. Low-loss moduli as well as low-sol fractions indicate that low-elastic moduli can be obtained without compromising the network's structure.

General information

State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering, Technical University of Denmark
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Fleury, C. (Ekstern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
Adhesion between Polydimethylsiloxane Layers by Crosslinking

Adhesion between two surfaces may be strongly improved by chemical crosslinking of the interfaces. Polydimethylsiloxane (PDMS) is a widely used polymer that has received considerable attention due to its unique properties, such as relatively low price, biocompatibility, flexibility, high thermal stability, and outstanding dielectric properties. The excellent performances of PDMS elastomers enable the realization of pneumatic, electromagnetic, and thermal actuators. In this work, two-layered PDMS films were adhered together by different mixtures of crosslinkers. The double-layered films were investigated by rheology and microscopy. The objective of this work was to create adhesion of two layers without destroying the original viscoelastic properties of the PDMS films.
Development of novel PDMS elastomers for dielectric electroactive polymers (DEAPs)

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
Number of pages: 1
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Event: Abstract from EPF 6th summer school, Gargnano, Italy.
Main Research Area: Technical/natural sciences
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Dielektrisk spektroskopi i aktion som nyttigt polymeranalyseværktøj
Dielektrisk spektroskopi er blevet langt mere tilgængeligt som karakteriseringsværktøj både offline og direkte tilsluttet forskelligt produktionsudstyr. Her gives en række eksempler på anvendelser, hvor ellers svært tilgængelig information er blevet langt nemmere at opnå vha. dielektrisk spektroskopi.

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Daugaard, A. E. (Intern), Skov, A. L. (Intern), Bøgelund, J. P. (Ekstern)
Pages: 20-21
Publication date: 2013
Main Research Area: Technical/natural sciences
Dielektrisk spektroskopi til karakterisering af plastmaterialer

Dielektrisk spektroskopi er blevet et vigtigt redskab i arbejde med polymere materialer. Her gives en introduktion til metoden dielektrisk spektroskopi og hvilke fænomener teknikken er baseret på med fokus på analyse af polymer systemer.

Dipolar cross-linkers for PDMS networks with enhanced dielectric permittivity and low dielectric loss

Dipole grafted cross-linkers were utilized to prepare polydimethylsiloxane (PDMS) elastomers with various chain lengths and with various concentrations of functional cross-linker. The grafted cross-linkers were prepared by reaction of two alkyne-functional dipoles, 1-ethynyl-4-nitrobenzene and 3-(4-((4-nitrophenyl)diazenyl)phenoxy)-prop-1-yn-1-ylum, with a synthesized silicone compatible azide-functional cross-linker by click chemistry. The thermal, mechanical and electromechanical properties were investigated for PDMS films with 0 to 3.6 wt% of dipole-cross-linker. The relative dielectric permittivity was found to increase by ~20% at only 0.46 wt% of incorporated dipole without significant changes in the mechanical properties. Furthermore, the dielectric losses were proved to be remarkably low while the electrical breakdown strengths were high.
Electrochemically driven ATRP applied for direct surface grafting of PEDOT

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State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Technical University of Denmark
Authors: Daugaard, A. E. (Intern), Hoffmann, C. (Ekstern)
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Event: Abstract from Nordic Polymer Days 2013, Helsinki, Finland.
Main Research Area: Technical/natural sciences
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High dielectric permittivity elastomers from well-dispersed expanded graphite in low concentrations

The development of elastomer materials with a high dielectric permittivity has attracted increased interest over the last years due to their use in for example dielectric electroactive polymers. For this particular use, both the electrically insulating properties - as well as the mechanical properties of the elastomer - have to be tightly controlled in order not to destroy favorable elastic properties by the addition of particles. In the following, expanded graphite in low concentrations (up to 5 wt%) are investigated as a possible candidate as filler materials in very soft elastomers, which by the addition of traditional fillers in the necessary amounts would either lose their stability or their softness. Furthermore the influence of several mixing procedures on the electrical and mechanical properties is investigated. © 2013 SPIE.

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Daugaard, A. E. (Intern), Hassouneh, S. S. (Intern), Kostrzewska, M. (Intern), Bejenariu, A. G. (Intern), Skov, A. L. (Intern)
Number of pages: 11
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Intelligente materialer som kunstige muskler og energi-hæstere

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
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Novel cross-linkers for PDMS networks for controlled and well distributed grafting of functionalities by click chemistry

An azide-containing, trifunctional vinyl cross-linker for silicone networks has been synthesized. The cross-linker has through Cu(i) catalyzed 1,3-cycloaddition been reacted with six different alkyne-containing chemical groups which each possess a particular functionality. The functional cross-linkers have been utilized to prepare novel polydimethylsiloxane (PDMS) networks. All functional cross-linkers were successfully incorporated into the networks and were demonstrated to be well distributed within the PDMS films. This was substantiated by fluorescence microscopy of a film prepared with the 4-methyl-umbelliferone containing cross-linker. TGA showed that a ferrocene functionality increased the thermal degradation temperature of PDMS. It was furthermore shown that the incorporation of only 0.25 wt% of the push-pull dipole, ethynyl-4-nitrobenzene, increased the dielectric permittivity of PDMS by 35%. The contact angle of PDMS films was increased from 108° to 116° by the introduction of a small poly(pentafluorostyrene) chain. Finally, 17α-ethynyl-1,3,5(10)-estratriene-3,17β-diol and 1-ethynyl-3,5-bis(trifluoromethyl)benzene were incorporated as examples of other functional groups. © 2013 The Royal Society of Chemistry.
Novel silicone compatible cross-linkers for controlled functionalization of PDMS networks
Polydimethylsiloxane (PDMS) elastomers are excellent materials for dielectric electroactive polymers (DEAPs) due to their high efficiency and fast response. PDMS suffers, however, from low dielectric permittivity and high voltages are therefore required when the material is used for DEAP actuators. In order to improve the dielectric properties of PDMS a novel system is developed where push-pull dipoles are grafted to a new silicone compatible cross-linker. The grafted cross-linkers are prepared by reaction of two different push-pull dipole alkynes as well as a fluorescent alkyne with the new azide-functional cross-linker by click chemistry. The dipole cross-linkers are used to prepare PDMS elastomers of various chains lengths providing different network densities. The functionalized cross-linkers are incorporated successfully into the networks and are well distributed as determined by the fluorescent functional cross-linker and fluorescence microscopy. The thermal, mechanical and electro-mechanical properties of PDMS elastomers of 0 wt% to 3.6 wt% of push-pull dipole cross-linker are investigated. An increase in the dielectric permittivity of 19 % at only 0.46 wt% of pure push-pull dipole is observed. Furthermore, the dielectric losses are found to be very low while the electrical breakdown strengths are high and adequate for DEAP applications. © 2013 SPIE.

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State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Madsen, F. B. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
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Reinforced poly(propylene oxide)- a very soft and extensible dielectric electroactive polymer
Poly(propylene oxide) (PPO), a novel soft elastomeric material, and its composites were investigated as a new dielectric electroactive polymer (EAP). The PPO networks were obtained from thiol-ene chemistry by photochemical crosslinking of 1,4-diallyl PPO with a tetra-functional thiol. The elastomer was reinforced with hexamethylenedisilazane treated fumed silica to improve the mechanical properties of PPO. The mechanical properties of PPO and composites thereof were investigated by shear rheology and stress–strain measurements. It was found that incorporation of silica particles improved the stability of the otherwise mechanically weak pure PPO network. Dielectric spectroscopy revealed high relative dielectric permittivity of PPO at 103 Hz of 5.6. The relative permittivity was decreased slightly upon addition of fillers, but remained higher than the commonly used acrylic EAP material VHB4910. The electromechanical actuation performance of both PPO and its composites showed properties as good as VHB4910 and a lower viscous loss.

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering, University of Pisa
Authors: Goswami, K. (Intern), Galantini, F. (Ekstern), Mazurek, P. S. (Intern), Daugaard, A. E. (Intern), Gallone, G. (Ekstern), Skov, A. L. (Intern)
Publication date: 2013
Main Research Area: Technical/natural sciences
Silicone resembling poly (propylene glycol) interpenetrating networks based on no pre-stretch as basis for electrical actuators

General information
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Stimuli-Adaptable Materials

The work presented in this Thesis deals with the development of a stimuli-adaptable polymer material based on the UV-induced dimerisation of cinnamic acid and its derivatives. It is in the nature of an adhesive to adhere very well to its substrate and therefore problems can arise upon removal of the adhesive. This is also known from skin adhesives where it is very undesirable to cause damage to the skin. The overall idea of this project was to resolve this problem by developing a material which could switch between an adhesive and a non-adhesive state. Switchable adhesion is known in the literature but the presented work has a new approach to the field by basing itself on the idea of developing a network into which a photo-active polymer is mixed and which function as an adhesive. Upon irradiation with UV-light for a short time a non-adhering inter-penetrating network material would be formed. Two simple models for the extent of reaction for the system are presented and show that the timescale for the reaction is minutes to hours. This was further investigated with IR-spectroscopy and UV-absorbance spectroscopy. UV-spectroscopy confirmed that a change in the material occurs upon irradiation with UV and that the reaction time is in the range of minutes. A number of polymer derivatives with cinnamic acid or cinnamylidene acetic acid were prepared and the material properties of these were studied before and after irradiation with UV-light. For the cinnamylidene acetic acid derivatised polymers a macroscopic change was observed upon dissolution of the irradiated compound. The irradiated polymers formed threads or fibres when exposed to water while the unexposed polymers dissolved as a hygroscopic powder. Cinnamic acid derivatised poly(ethylene glycol) (PEG) was studied in detail and three different polymers were derivatised, namely a 4-armed star PEG (Mn = 2000 g/mol), a short linear PEG (Mn = 1000 g/mol) and a long linear PEG (Mn = 4000 g/mol). The derivatised polymers were mixed to create three different photo-active materials and these were investigated with rheology before and after irradiation with UV-light for one hour. It was observed that the largest change occurred for the system consisting solely of the cinnamic acid derivatised 4-armed star PEG. The development of the material properties of this material was studied in details by exposing the compound to UV-irradiation for up to 120 h and determining the rheological properties after the exposure. It was found that approx. 24 hours was needed to form a manageable film and that approx. 70 hours were needed to obtain stable rheological properties. The exposure times were larger than expected but it was assumed that this would be resolved by preparation of the inter-penetrating network materials. A number of inter-penetrating network materials where both the permanent Network as well as the switching segment was made up of PEG-polymers were prepared. It was found that for a material with relatively long chains in both permanent Network (Mn = 10000 g/mol) and switching segment (Mn = 15000 g/mol) no changes occurred upon exposure to UV-light. It is expected that this is because Mn of polymers is above the molecular entanglement weight. Inter-penetrating network materials with Mn = 4000 g/mol in the permanent network were prepared. Initially a linear photo-active PEG was mixed into the material. This material exhibited a decrease in the values for G and G after irradiation with UV-light for 30 minutes. The reason for the decrease in the two rheological parameters is unclear but the change encouraged further work with this type of systems. Two inter-penetrating network materials with the star-shaped cinnamic acid derivatised PEG as switching segment were prepared and irradiated with UV-light for 72 hours. The network with \( r = 0.75 \) in the permanent matrix proved the expectations by clearly showing a solvent effect when the photo-active polymer was introduced into the permanent network. In addition a significant increase of G and G was observed after 72 h of irradiation with UV-light proving the formation of a second network consisting of the photo-active polymers. A network with \( r = 0.5 \) in the permanent matrix was also investigated but gave very different results due to the lower value for \( r \). The applied \( r \)-value is significantly closer to the critical \( r_c \)-value and thus resulted in problems with the film formation. The data showed that the secondary network dominates the rheological properties of this network. A material with shorter chains in the permanent network (Mn = 1000 g/mol) was also investigated but showed no change after irradiation with UV-light for 15 minutes. This is related to the stiffness of permanent matrix. First steps to creating an inter-penetrating network with two different polymers were taken by incorporating the cinnamic acid derivatised PEG-stars into a poly(propylene oxide) network. However exposure to UV-light did not result in any changes of the material properties. It was also tested if the photo-active PEG could be incorporated
into a poly(dimethyl siloxane) network, but the addition of the photo-active PEG resulted in complete hindrance of the cross-linking of the poly(dimethyl siloxane). A number of problems were identified throughout the work, primarily concerning the mismatch between the expected exposure time needed to induce changes in the materials and the exposure time observed experimentally. This can partially be explained by mobility of the polymers and concentration of the photo-active cinnamic acid. Studies presented in the literature show that the position of the cinnamic acid groups is important for the dimerisation to occur. The nature of polymers makes encounters between end groups less likely and this affects the dimerisation. Furthermore, an NMR-study showed formation of the cis-isomer of cinnamic acid. The isomerisation of cinnamic acid only occurs if dimerisation is hindered. This underlines that the circumstances are not ideal for dimerisation.

**General information**

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering, CHEC Research Centre
Authors: Frankær, S. M. G. (Intern), Skov, A. L. (Intern), Kiil, S. (Intern), Daugaard, A. E. (Intern)
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**Adhesion Between Poly(dimethylsiloxane) Layers**

Different adhesion methods of poly(dimethylsiloxane) (PDMS) layers were studied with respect to adhesional force and the resulting rheology of the two-layered PDMS films were investigated. The role of adhesion between PDMS layers on the performances of two-layer structures was studied with peel strength test and by SEM pictures. The rheology of the double-layered compared to the monolayer films changed in some cases which indicates that the adhesion process needs to be carefully introduced in order not to alter the final properties.

**General information**

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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Yu, L. (Intern), Daugaard, A. E. (Intern), Skov, A. L. (Intern)
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**A Platform for Functional Conductive Polymers**

Conductive polymers have been studied extensively during recent years. In order to broaden the application field of conductive polymers different methods have been tested and recently an azide functional poly(3,4-ethylenedioxythiophene) (PEDOT-N3) was developed(1, 2). The azide functional conductive polymer can be postpolymerization functionalized to introduce a large number of functionalities through click chemistry(3).

Through selection of reaction conditions it is possible control the depth of the reaction into the polymer film to the upper surface or the entire film(4). Thus a conductive polymer can be prepared with a subsurface layer of highly conductive polymer where only the upper surface has been functionalized with functional groups to ensure selectivity of the surface layer for e.g. interaction with specific biospecies. The conductive polymer can be patterned using selective etching, which enables preparation of e.g. interdigitated electrodes or other surface structures. The electrodes have been applied in controlled localized click reactions through “electroclick” reactions(5). This enables preparation of both highly functional electrodes as well as gradient surfaces(6). The system is very versatile in all dimensions and structures and allows for preparation of conductive polymers with very specific properties. Recent results on a grafting from method to modify the surface properties will be presented.

**General information**

State: Published
A Versatile Toolbox for Preparation of Functional Conductive Polymers

General information
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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Department of Micro- and Nanotechnology, Polymer Microsystems for Cell Processing
Authors: Daugaard, A. E. (Intern), Hoffmann, C. (Ekstern), Lind, J. U. (Intern), Hansen, T. S. (Intern), Larsen, N. B. (Intern), Hvilsted, S. (Intern)
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Bimodal Networks as Candidates for Electroactive Polymers

An alternative network formulation method was adopted in order to obtain a different type of silicone based elastomeric systems - the so-called bimodal networks - using two vinyl-terminated polydimethyl siloxanes (PDMS) of different molecular weight, a labelled crosslinker (3 or 4-functional), and a platinum-catalyzed hydrosilylation reaction between the three reactants3. The crosslinking reaction was initiated by mixing different amounts of short PDMS chains and long PDMS chains with the stoichiometric amount of the crosslinker in a series of mixing schemes. We visualize how the short chains organize themselves between the long chains and show how this leads to unexpectedly good properties for DEAP purposes due both to the low extensibility of the short chains that attach strongly the long chains and to the extensibility of the last ones that retards the rupture process.

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Development of new PDMS based materials for dielectric electroactive polymers (DEAPs) as actuators and generators

General information
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Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
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Publication date: 2012
Functionalization of PEDOT by Click Chemistry and ATRP

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conductive polymer which has received increasing attention and many developments have been investigated. PEDOT has been applied in many different areas such as biosensors or polymer solar cells. This work presents a modification of PEDOT films through Click Chemistry with alkynes followed by activator regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) to develop PEDOT films with anti-fouling properties through application of a crosslinked surface of polystyrene PS N3.

Influence of micro- and nanofillers on electro-mechanical performance of silicone EAPs

The effect of different fillers on the mechanical and dielectric properties of soft elastomers has been investigated. It was found that the addition of a small amount of silica fillers would increase the Young’s modulus significantly but not simultaneously increase the tear strength sufficiently for processing as thin films. Addition of nanoclay and barium titanate nanoparticles to the soft elastomers was shown to be very favorable for the enhancement of the dielectric properties without increasing the Young’s modulus significantly and could be used for DEAP material in e.g. microprocessing where the tear strength is not crucial for processing. However, for elastomer film processing it is suggested that a combination of the nanoclay or barium titanate with either silica particles or bimodal networks would give the right tear strength together with the desired increased dielectric permittivity.
Micropatterning of Functional Conductive Polymers with Multiple Surface Chemistries in Register

A versatile procedure is presented for fast and efficient micropatterning of multiple types of covalently bound surface chemistry in perfect register on and between conductive polymer microcircuits. The micropatterning principle is applied to several types of native and functionalized PEDOT (poly(3,4-ethylenedioxythiophene)) thin films. The method is based on contacting PEDOT-type thin films with a micropatterned agarose stamp containing an oxidant (aqueous hypochlorite) and...
applying a nonionic detergent. Where contacted, PEDOT not only loses its conductance but is entirely removed, thereby locally revealing the underlying substrate. Surface analysis showed that the substrate surface chemistry was fully exposed and not affected by the treatment. Click chemistry could thus be applied to selectively modify re-exposed alkyne and azide functional groups of functionalized polystyrene substrates. The versatility of the method is illustrated by micropatterning cell-binding RGD-functionalized PEDOT on low cell-binding PMOXA (poly(2-methyl-2-oxazoline)) to produce cell-capturing microelectrodes on a cell nonadhesive background in a few simple steps. The method should be applicable to a wide range of native and chemically functionalized conjugated polymer systems.

**General information**

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Scopus rating (2014): SJR 1.816 SNIP 1.391 CiteScore 4.59
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Scopus rating (2012): SJR 2.177 SNIP 1.382 CiteScore 4.37
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Scopus rating (2011): SJR 2.051 SNIP 1.357 CiteScore 4.42
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 2.148 SNIP 1.4
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Scopus rating (2009): SJR 2.156 SNIP 1.351
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Scopus rating (2007): SJR 2.449 SNIP 1.434
New Cross-linkers for PDMS Networks

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Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
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Publication date: 2012
Event: Abstract from 49th Nordic Polymer Days 2012, Copenhagen, Denmark.
Main Research Area: Technical/natural sciences
Electronic versions:
Abstract Frederikke Bahrt.pdf
Links:
http://www.npd2012.dk/
Source: dtu
Source-ID: u::3782
Publication: Research › Conference abstract for conference – Annual report year: 2012

Novel silicone compatible cross-linkers for controlled and well distributed functionalization of PDMS networks

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Center for Energy Resources Engineering
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
Number of pages: 1
Publication date: 2012
Main Research Area: Technical/natural sciences
Electronic versions:
prod21367841541910_Abstract_for_Annual_Polymer_day_2012.pdf
Source: dtu
Source-ID: u::7505
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2013
Poly(ethylene-co-butylene) functionalized multi walled carbon nanotubes applied in polypropylene nanocomposites

A novel functionalized multi walled carbon nanotube (MWCNT) was prepared through grafting with α-azido-poly(ethylene-co-butylene) (PEB-N3). The PEB-N3 was prepared through a two step procedure and grafted onto an industrial grade multi walled carbon nanotube (MWCNT) through a highly efficient nitrene addition. This novel nano filler was melt mixed into polypropylene (PP) and the composite was characterized by FT-IR spectroscopy, Raman spectroscopy, Scanning Electron Microscopy (SEM), Rheology and Dielectric Relaxation Spectroscopy (DRS). The analyses showed that composites with the novel filler had a high degree of discharge from the surface and higher conductivity compared to the pristine filler, illustrating an efficient conductive network in the composites. The composites showed low percolation thresholds of 0.3wt.% (0.15vol.%) as well as improved stability at a range of temperatures from 25–135°C.

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Danish Technological Institute
Authors: Daugaard, A. E. ( Intern), Jankova Atanasova, K. ( Intern), Marín, J. M. R. ( Intern), Bøgelund, J. ( Forskerdatabase), Hvilsted, S. ( Intern)
Pages: 743-750
Publication date: 2012
Main Research Area: Technical/natural sciences

Publication information
Journal: European Polymer Journal
Volume: 48
Issue number: 4
ISSN (Print): 0014-3057
Ratings:
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 1.059 SNIP 1.279 CiteScore 3.75
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.032 SNIP 1.36 CiteScore 3.58
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.117 SNIP 1.494 CiteScore 3.35
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.093 SNIP 1.689 CiteScore 3.43
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.076 SNIP 1.749 CiteScore 2.99
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.108 SNIP 1.858 CiteScore 3.03
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.298 SNIP 1.569
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.165 SNIP 1.356
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 1.118 SNIP 1.293
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.15 SNIP 1.374
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.092 SNIP 1.472
Role of stoma effluent on adhesion between skin-friendly adhesives and skin

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Coloplast Danmark A/S
Authors: Ravni, C. (Ekstern), Hansen, K. (Ekstern), Daugaard, A. E. (Intern), Skov, A. L. (Intern)
Number of pages: 1
Publication date: 2012
Event: Abstract from 49th Nordic Polymer Days 2012, Copenhagen, Denmark.
Main Research Area: Technical/natural sciences

Udvikling af materialer til kunstige muskler
Ultratynne top-præsterende højtalere, bølgeenergi-generatorer med energiproduktion i enorme mængder, aktuatorer uden standby-energiforbrug og bløde deformerbare kunstige muskler kan måske snart realiseres vha. dielektriske elektroaktive polymerer (DEAP).

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Bahrt, F. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Skov, A. L. (Intern)
Pages: 48-51
Publication date: 2012
Main Research Area: Technical/natural sciences
Unimodal and bimodal networks performance as dielectric electroactive polymers (DEAPs)

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Authors: Bejenariu, A. G. (Intern), Daugaard, A. E. (Intern), Skov, A. L. (Intern)
Publication date: 2012
Event: Abstract from 49th Nordic Polymer Days 2012, Copenhagen, Denmark.
Main Research Area: Technical/natural sciences
Electronic versions:
Abstract_NPD_31May2012KBH_1_.pdf
Source: dtu
Source-ID: u::3655
Publication: Research › Conference abstract for conference – Annual report year: 2012

Cinnamic Acid Derivatised Poly(Ethylene Glycol) as a Bioinspired UV-Adaptable Material

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, CHEC Research Centre, Technical University of Denmark
Publication date: 2011
Main Research Area: Technical/natural sciences
Electronic versions:
Abstract_SarahMariaFrankaer.pdf
Source: orbit
Source-ID: 278470
Publication: Research › Conference abstract for conference – Annual report year: 2011

Dielectric Properties of Poly(ethylene-co-butylene) Modified MWCNT/Polypropylene Composites

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Danish Technological Institute
Authors: Daugaard, A. E. (Intern), Jankova Atanasova, K. (Intern), Begelund, J. (Ekstern), Marin, J. (Ekstern), Hvilsted, S. (Intern)
Publication date: 2011
Main Research Area: Technical/natural sciences
Electronic versions:
POLIMEROSTEMPLATE_ABSTRACT_EPF01238.pdf
Source: orbit
Source-ID: 278291
Publication: Research › Conference abstract for conference – Annual report year: 2011
Directing functional chemistries on micropatterned conducting polymers for all-polymer cell analysis microsystems

Micrometer scale electrical circuits of PEDOT (poly(3,4-dioxythiophene)) were created by locally oxidizing PEDOT thin films with an agarose stamp containing the oxidizing agent NaOCl. The oxidized PEDOT was removed completely by applying detergents. The process was sufficiently mild that chemical groups on the underlying substrate, such as azides or alkynes, were preserved for subsequent specific functionalization. Moreover entire PMOXA (poly(2-methyl-2-oxazoline)) films preventing cell binding could be hidden below the PEDOT and be re-exposed upon stamping, allowing for cell capturing microelectrodes on a cell non-adhesive background. Chemically functionalized PEDOT types permitted the introduction of multiple additional types of micropatterned chemistry.

General information
State: Published
Organisations: Department of Micro- and Nanotechnology, The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Eidgenössische Technische Hochschule
Authors: Lind, J. U. (Intern), Daugaard, A. E. (Intern), Andresen, T. L. (Intern), Acikgöz, C. (Ekstern), Textor, M. (Ekstern), Larsen, N. B. (Intern)
Publication date: 2011
Event: Poster session presented at 15th International Conference on Miniaturized Systems for Chemistry and Life Sciences, Seattle, WA, United States.
Main Research Area: Technical/natural sciences
Surface modification, PEDOT, Conducting polymers, Micropatterning, Click chemistry
Source: orbit
Source-ID: 318458
Publication: Research - peer-review › Poster – Annual report year: 2011
Laviosa Chimica Mineralia, Italy) by the synthesized charged block copolymer, which was performed in water. Modified nanoclays with 2.5 to 8.0 wt.-% of the quaternized PEB-b-PDMAEMA35 were prepared. The exfoliation and intercalation was studied by XRD. Rheological measurements of either aq. solutions of the charged block copolymers or PP master batches with various amounts of the modified MMT were performed. Tensile tests of NCs show similar behavior, but SAXS reveals change in the nanostructure. According to the structural data derived from SAXS [4] the MMT acts like a nucleating agent to the PP that starts competitive nucleation of crystallites in the PP during manufacturing. Consequently, the PP crystallites in the composites are small and imperfect. This means that the self-reinforcement of the PP (by its crystallites) is replaced by alien-reinforcement (of the MMT). Furthermore, the results from the impact strength and cyclic test of the prepared PP nanocomposites [3] are promincing.

Influence of micro- and nanofillers on DEAP performance

The formulation of dielectric electroactive polymers (DEAP) is a challenging task as the elastomer part of DEAP is a multi-component system with strict requirements to the electromechanical performance. In traditional formulated products such as paints there is a huge variety of filler materials available and the filler particles are used both to lower the price and to increase the performance of the material. In DEAP there is a strong interplay between the electrical and mechanical properties as one property may be improved and another worsened when changing the formulation so in many cases optimization of the properties ends in a trade-off of some kind. In this study we focus on the addition of well-known commercially available filler particles and evaluate their performance in elastomers applied for DEAP since the price of the fillers also have to be taken into account when formulating. The effect of particle size and particle size distribution on the electrical and viscoelastic properties is investigated. Both nano- and microscale particles of different compositions are mixed with a platinum cured silicone elastomer matrix [1] in different combinations, and the dielectric and viscoelastic properties are measured. The dielectric properties are improved mainly by decreasing the particle size as was also shown by Kofod et al [2] for acrylic networks whereas the elastic properties are influenced in a less trivial way. The filler particles increase the storage modulus and make the films easier to handle but the formulation of the ‘raw’ silicone matrix has to be modified as the filler particles in some instances interact with the polymers and hence require a changed stoichiometry to ensure complete reaction of both reactive species in the silicone matrix.

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, University of Hamburg, Aalborg University
Authors: Jankova Atanasova, K. (Intern), Daugaard, A. E. (Intern), Stribeck, N. (Ekstern), Zeinolebadi, A. (Ekstern), Sari, M. G. (Ekstern), Potarniche, C. (Ekstern), Jensen, E. A. (Ekstern), Christiansen, J. D. C. (Ekstern), Hvilsted, S. (Intern)
Publication date: 2011
Main Research Area: Technical/natural sciences
Electronic versions:
Katja.pdf
Links:

Bibliographical note
Poster presentation.
Source: orbit
Source-ID: 279471
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2011

Influence of micro- and nanofillers on DEAP performance

The formulation of dielectric electroactive polymers (DEAP) is a challenging task as the elastomer part of DEAP is a multi-component system with strict requirements to the electromechanical performance. In traditional formulated products such as paints there is a huge variety of filler materials available and the filler particles are used both to lower the price and to increase the performance of the material. In DEAP there is a strong interplay between the electrical and mechanical properties as one property may be improved and another worsened when changing the formulation so in many cases optimization of the properties ends in a trade-off of some kind. In this study we focus on the addition of well-known commercially available filler particles and evaluate their performance in elastomers applied for DEAP since the price of the fillers also have to be taken into account when formulating. The effect of particle size and particle size distribution on the electrical and viscoelastic properties is investigated. Both nano- and microscale particles of different compositions are mixed with a platinum cured silicone elastomer matrix [1] in different combinations, and the dielectric and viscoelastic properties are measured. The dielectric properties are improved mainly by decreasing the particle size as was also shown by Kofod et al [2] for acrylic networks whereas the elastic properties are influenced in a less trivial way. The filler particles increase the storage modulus and make the films easier to handle but the formulation of the ‘raw’ silicone matrix has to be modified as the filler particles in some instances interact with the polymers and hence require a changed stoichiometry to ensure complete reaction of both reactive species in the silicone matrix.

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Skov, A. L. (Intern), Bejenariu, A. G. (Intern), Daugaard, A. E. (Intern)
Publication date: 2011
Event: Abstract from 6th World Congress on Biomimetics, Artificial Muscles and Nano-Bio, Cergy-Pontoise, France.
Main Research Area: Technical/natural sciences
Electronic versions:
anadeladegaardskov_biomimetics2011-2.pdf
Links:
http://biomimetics2011.u-cergy.fr/

Bibliographical note
Oral presentation.
Source: orbit
Source-ID: 279778
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2011
**Influence of micro- and nanofillers on electro-mechanical performance of silicone EAPs**

A well-known technique to improve the tear strength of rubbers is to add micro- or nanofillers. The effects of different micro- and nanofillers on the electro-mechanical behavior of silicone based dielectric elastomer are studied in this work. Several types of fillers and varied loadings are used to increase the overall permittivity of the silicone networks. The effect of particle size and particle size distribution on the electrical and viscoelastic properties is investigated. The aim of the paper is to find the right filler and the appropriate concentration for a suitable EAP material, such that an optimized formulation schema can be proposed.

**Microwave assisted click chemistry on a conductive polymer film**

Microwave (MW) irradiation has been used to accelerate the functionalization of an azide functional poly(3,4-ethylenedioxythiophene) film by click chemistry. The absorption of MW energy by the conductive polymer has been exploited for localized activation of the reaction on the polymer surface. By use of an alkyne modified fluorescein derivative the reaction conditions have been optimized in a conventional MW oven, enabling the use of different sizes of substrates. The optimization resulted in a reduction of reaction times of approximately 20h to only 2min for bulk film functionalization. The method has been applied for anchoring of the chelating agent nitrilotriacetic acid (NTA) on the conductive polymer. The chelating linkage ability of NTA on the surface was investigated through a sandwich ELISA study confirming the selective bonding of a histidine tagged protein.
Multi Walled Carbon Nanotubes Functionalized by a Solvent Free Method for Application in Polypropylene Nanocomposites

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Aalborg University
Authors: Daugaard, A. E. (Intern), Jankova Atanasova, K. (Intern), Christiansen, J. D. C. (Ekstern), Hvilsted, S. (Intern)
Publication date: 2011
Main Research Area: Technical/natural sciences
Electronic versions:
AED_abstact_NPD_2011.pdf
Source: orbit
Source-ID: 278295
Publication: Research › Conference abstract for conference – Annual report year: 2011

New Cross-linkers for PDMS Networks

General information
Solvent Composition Directing Click-Functionalization at the Surface or in the Bulk of Azide-Modified PEDOT

Thin films of the conducting polymer poly(3,4-(1-azidomethylethylene)dioxythiophene) tosylate (PEDOT−N3) can be functionalized by reaction with alkynated reagents in aqueous solutions. Reaction in pure water resulted in surface specific modification of PEDOT−N3 films, whereas both surface and bulk reaction was achieved in solvent mixtures of water and DMSO. These reaction patterns were confirmed by a combination of AFM and XPS measurements on the front- and backside of the film. The phenomenon is attributed to a strong dependence of the swelling of PEDOT−N3 on the solvent mixture used. Liquid AFM studies showed increasing film thickness with increasing DMSO content, with the measured thickness in pure DMSO being >250% of the thickness in pure water. A similar, but less pronounced, behavior was observed for unmodified poly(3,4-ethylenedioxythiophene) tosylate (PEDOT). High-density grafting of a number of alkynated compounds onto PEDOT−N3 was achieved via controlled swelling of the polymer. In particular, grafting of alkynated poly(ethylene glycol) (PEG) was optimized to minimize protein adsorption to the conductive polymer surface. Intermediate swelling of PEDOT−N3 during the reaction, using ~50% DMSO, resulted in the formation of a dense PEG surface layer with low protein adhesiveness without adversely affecting the conductive properties of the film.
Complex Surface Concentration Gradients by Stenciled "Electro Click Chemistry"

Complex one- or two-dimensional concentration gradients of alkylnated molecules are produced on azidized conducting polymer substrates by stenciled "electro click chemistry". The latter describes the local electrochemical generation of catalytically active Cu(I) required to complete a "click reaction" between alkynes and azides at room temperature. A stencil on the counter electrode defines the shape and multiplicity of the gradient(s) on the conducting polymer substrate, while the specific reaction conditions control gradient steepness and the maximum concentration deposited. Biologically active ligands including cell binding peptides are patterned in gradients by this method without losing their biological function or the conductivity of the polymer.

General information
State: Published
Organisations: Department of Micro- and Nanotechnology, Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Colloids and Biological Interfaces Group, Self-organizing materials for nanotechnology Section
Authors: Hansen, T. S. (Intern), Lind, J. U. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Andresen, T. L. (Intern), Larsen, N. B. (Intern)
Pages: 16171-16177
“Electro-Click” on Conducting Polymer Films

An azide substituted 3,4-ethylenedioxythiophene monomer is polymerised to yield a PEDOT like polymer with available azide groups (Figure 1). The azide groups enable post polymerization functionalization of the conducting polymer using a 1,3 dipolar cycloaddition reaction – also denoted “click chemistry”. This facilitates the addition of compounds that can otherwise not withstand the polymerization conditions. Several biological active molecules have been attached and tested on the films. Furthermore conducting polymer microelectrodes can electrochemically generate the catalyst required for their own functionalization with high spatial resolution. Interdigitated microelectrodes prepared from the azide-containing conducting polymer were selectively functionalized in sequence by two alkyne-modified fluorophores by control of the applied potentials. “Electro-click” on conducting polymer films shows the potential for being an important platform for biological devices and sensors.

General information
State: Published
Organisations: Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology, The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Hansen, T. S. (Intern), Lind, J. U. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Larsen, N. B. (Intern)
Publication date: 2010
Event: Abstract from International Conference on Science and Technology of Syntetic Metals 2010, Kyoto, Japan.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 265308
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2010

Microwave Assisted Functionalization of the Conductive Polymer Poly(3,4-ethylenedioxythiophene) by Copper Catalyzed Cycloaddition

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology
Authors: Daugaard, A. E. (Intern), Hansen, T. S. (Intern), Larsen, N. B. (Intern), Hvilsted, S. (Intern)
Publication date: 2010

Host publication information
Title of host publication: Nordic Polymer Days 2009
Main Research Area: Technical/natural sciences
Conference: Nordic Polymer Days 2009, Copenhagen, Denmark, 25/05/2009 - 25/05/2009
Source: orbit
Source-ID: 255756
Publication: Research - peer-review › Article in proceedings – Annual report year: 2009

Novel UV Initiator for Functionalization of Multiwalled Carbon Nanotubes by Atom Transfer Radical Polymerization Applied on Two Different Grades of Nanotubes

A novel nonoxidative method for preparation of functionalized multiwalled carbon nanotubes (MWCNT) has been developed based on a UV sensitive initiator for atom transfer radical polymerization (ATRP). The method has been investigated with respect to ligands and polymerization time for the preparation of polystyrene functionalized MWCNT. It was found that pentamethyldiethylenetriamine (PMDETA) gave superior results with higher loading in shorter polymerization time. A comparative study of the method applied on two different grades of nonoxidized MWCNT has been performed, illustrating large differences in reactivity and polymer loading, underlining the importance of the choice of MWCNT starting material. In addition to styrene, also poly(ethylene glycol) methacrylate (PEGMA) was shown to polymerize from the surface of the MWCNT. Finally, initial results from composites of polystyrene or polyphenylenesulfide are presented.

General information
State: Published
Organisations: Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology, The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Hansen, T. S. (Intern), Lind, J. U. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Larsen, N. B. (Intern)
Publication date: 2010
Polystyrene Functionalization of an Industrial Grade of Multi Walled Carbon Nanotubes by Atom Transfer Radical Polymerization

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Hvilsted, S. (Intern), Jankova Atanasova, K. (Intern), Daugaard, A. E. (Intern)
Publication date: 2010
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 274682
Publication: Research - peer-review › Paper – Annual report year: 2010

Dendronized macromonomers for three-dimensional data storage
A series of dendritic macromonomers have been synthesized and utilized as the photoactive component in holographic storage systems leading to high performance, low shrinkage materials.

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Khan, A. (Ekstern), Daugaard, A. E. (Intern), Bayles, A. (Ekstern), Koga, S. (Ekstern), Miki, Y. (Ekstern), Sato, K. (Ekstern), Enda, J. (Ekstern), Hvilsted, S. (Intern), Stucky, G. D. (Ekstern), Hawker, C. J. (Ekstern)
Pages: 425-427
Publication date: 2009
Main Research Area: Technical/natural sciences
Publication information
Journal: Chemical Communications
Issue number: 4
ISSN (Print): 1359-7345
Ratings:
Dendronized Macromonomers for Volume Holography

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Daugaard, A. E. (Intern), Kahn, A. (Ekstern), Hawker, C. (Ekstern), Hvilsted, S. (Intern)
Publication date: 2009

Host publication information
Title of host publication: 6th International Dendrimer Symposium, Book of Abstracts
Place of publication: Stockholm, Sweden
Main Research Area: Technical/natural sciences
Conference: Dendrimer Symposium, 01/01/2009
Source: orbit
Source-ID: 255766
Publication: Research - peer-review › Article in proceedings – Annual report year: 2009

Responsive Materials by Click Functionalization of the Conductive Polymer Poly(3,4-ethylenedioxythiophene)

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology
Authors: Daugaard, A. E. (Intern), Hansen, T. S. (Intern), Larsen, N. B. (Intern), Hvilsted, S. (Intern)
Publication date: 2009

Host publication information
Title of host publication: EUPOC2009
Main Research Area: Technical/natural sciences
Conference: EUPOC2009 - EPF Europolymer Conference "Click" - Methods in Polymer and Materials Science, Gargnano, Italy, 01/01/2009
Source: orbit
Source-ID: 255761
Publication: Research - peer-review › Article in proceedings – Annual report year: 2009

Spatially Selective Functionalization of Conducting Polymers by "Electroclick" Chemistry
Conducting polymer microelectrodes can electrochemically generate the catalyst required for their own functionalization by "click chemistry" with high spatial resolution. Interdigitated microelectrodes prepared from an azide-containing conducting polymer are selectively functionalized in sequence by two alkyne-modified fluorophores by control of the applied potentials.

General information
State: Published
Organisations: Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology, The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Hansen, T. S. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Larsen, N. B. (Intern)
Pages: 4483
Publication date: 2009
Main Research Area: Technical/natural sciences

Publication information
Journal: Advanced Materials
Volume: 21
Issue number: 44
ISSN (Print): 0935-9648
Ratings:
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 17.79
Web of Science (2016): Indexed yes
Unique Sensor Possibilities by "Click" Modifications of a Conducting Polymer

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology
Authors: Hvilsted, S. (Intern), Daugaard, A. E. (Intern), Hansen, T. S. (Intern), Larsen, N. B. (Intern)
Publication date: 2009

Host publication information
Title of host publication: European Polymer Congress, Book of Abstracts
Main Research Area: Technical/natural sciences
Conference: European Polymer Congress, Graz, Austria, 01/01/2009
Source: orbit
Source-ID: 255768
Publication: Research - peer-review › Article in proceedings – Annual report year: 2009

Conductive Polymer Functionalization by Click Chemistry
Click chemistry is used to obtain new conductive polymer films based on poly(3,4-ethylenedioxythiophene) (PEDOT) from a new azide functional monomer. Postpolymerization, 1,3-dipolar cycloaditions in DMF, using a catalyst system of CUS04 and sodium ascorbate, and different alkynes are performed to functionalize films of PEDOT-N3 and copolymers prepared from EDOT-N3 and 3,4-ethylenedioxythiophene (EDOT). This approach enables new functionalities on PEDOT
that could otherwise not withstand the polymerization conditions. Reactions on the thin polymer films have been optimized using an alkynated fluorophore, with reaction times of ~20 h. The applicability of the method is illustrated by coupling of two other alkynes: a short chain fluorocarbon and a MPEG 5000 to the conductive polymer; this alters the advancing water contact angle of the surface by +20° and -20°/-25°, respectively. The targeted chemical surface modifications have been verified by X-ray photoelectron spectroscopy analysis.

**General information**

State: Published

Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, Risø National Laboratory for Sustainable Energy

Authors: Daugaard, A. E. (Intern), Hvilsted, S. (Intern), Hansen, T. S. (Intern), Larsen, N. B. (Intern)

Pages: 4321-4327

Publication date: 24 Jun 2008

Main Research Area: Technical/natural sciences

**Publication information**

Journal: Macromolecules

Volume: 41

Issue number: 12

ISSN (Print): 0024-9297

Ratings:

BFI (2017): BFI-level 2

Web of Science (2017): Indexed Yes

BFI (2016): BFI-level 2

Scopus rating (2016): CiteScore 5.76 SJR 2.557 SNIP 1.507

Web of Science (2016): Indexed yes

BFI (2015): BFI-level 2

Scopus rating (2015): SJR 2.407 SNIP 1.638 CiteScore 5.82

Web of Science (2015): Indexed yes

BFI (2014): BFI-level 2

Scopus rating (2014): SJR 2.534 SNIP 1.721 CiteScore 5.83

Web of Science (2014): Indexed yes

BFI (2013): BFI-level 2

Scopus rating (2013): SJR 2.576 SNIP 1.754 CiteScore 6.09

ISI indexed (2013): ISI indexed yes

Web of Science (2013): Indexed yes

BFI (2012): BFI-level 2

Scopus rating (2012): SJR 2.779 SNIP 1.58 CiteScore 5.35

ISI indexed (2012): ISI indexed yes

Web of Science (2012): Indexed yes

BFI (2011): BFI-level 2

Scopus rating (2011): SJR 2.556 SNIP 1.593 CiteScore 5.15

ISI indexed (2011): ISI indexed yes

Web of Science (2011): Indexed yes

BFI (2010): BFI-level 2

Scopus rating (2010): SJR 2.51 SNIP 1.51

Web of Science (2010): Indexed yes

BFI (2009): BFI-level 2

Scopus rating (2009): SJR 2.962 SNIP 1.533

Web of Science (2009): Indexed yes

BFI (2008): BFI-level 2

Scopus rating (2008): SJR 2.819 SNIP 1.54

Web of Science (2008): Indexed yes

Scopus rating (2007): SJR 3.102 SNIP 1.613

Web of Science (2007): Indexed yes

Scopus rating (2006): SJR 2.987 SNIP 1.714
A Novel Approach to XPS Characterisation of ‘Click’ Surface Chemistry, More Information Less Damage

General information
State: Published
Organisations: Department of Micro- and Nanotechnology, Polymer Microsystems for Cell Processing, Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Thermo Fisher Scientific
Authors: Nunney, T. (Ekstern), Larsen, N. B. (Intern), White, R. (Ekstern), Hansen, T. S. (Intern), Daugaard, A. E. (Intern), Hvilsted, S. (Intern)
Publication date: 2008
Event: Abstract from AVS 55th International Symposium & Exhibition, Boston, MA, United States.
Main Research Area: Technical/natural sciences
Electronic versions:
AVS 55th International Symposium & Exhibition, Paper BI-WeA3.htm

Bibliographical note
Presenter: T.S.Nunney
Source: dtu
Source-ID: u::4548
Publication: Research › Conference abstract for conference – Annual report year: 2008

Conductive Polymer Functionalization by Click Chemistry

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Micro and Nano Engineering Section, Department of Micro- and Nanotechnology
Authors: Daugaard, A. E. (Intern), Hansen, T. (Ekstern), Larsen, N. B. (Intern), Hvilsted, S. (Intern)
Publication date: 2008
Event: Abstract from 4th STIPOMAT Conference, Lacanau, France.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 235076
Publication: Research › Conference abstract for conference – Annual report year: 2008

Functionalized Conducting Polymers for Cell Processing

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Polymer Microsystems for Cell Processing Group, Polymer Micro and Nano Engineering Section, Department of Micro- and
The influence of pendant carboxylic acid loading on surfaces of statistical poly(4-hydroxystyrene)-co-styrene) Copolymers of 4-tert-butoxystyrene (tBS) and styrene (5) have been prepared by free radical copolymerization and the copolymer ratios of TtBS == 0.97 and Ts == 1.12 have been determined by the Kelen-Tiidos method. After deprotection to 4-hydroxystyrene, alkynes were introduced by a Williamson ether synthesis with propargyl bromide and the copolymers were functionalized with pendant aliphatic or aromatic carboxylic acids by click chemistry. Differential scanning calorimetry of the copolymers demonstrates the large influence on Tg of the different functional groups and the backbone composition. In particular, aliphatic and aromatic pendant groups differ by 92°C in Tg. Contact angle measurements on spin coated films have shown a maximum effect of the functional groups in the advancing contact angle at a 75/100 copolymer loading. In addition to this, X-ray photoelectron spectroscopy shows the presence of acid groups on the surface.

General information
State: Published
Organisations: The Danish Polymer Centre, Department of Chemical and Biochemical Engineering
Authors: Daugaard, A. E. (Intern), Hvilsted, S. (Intern)
Pages: 1119-1125
Publication date: 2008
Main Research Area: Technical/natural sciences

Publication information
Journal: Macromolecular Rapid Communications
Volume: 29
Issue number: 12
ISSN (Print): 1022-1336
Ratings:
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 1.689 SNIP 0.946 CiteScore 4.19
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.795 SNIP 1.069 CiteScore 4.66
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.807 SNIP 1.136 CiteScore 4.72
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.762 SNIP 1.137 CiteScore 4.78
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 2.09 SNIP 1.239 CiteScore 4.7
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.999 SNIP 1.13 CiteScore 4.47
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 2.04 SNIP 1.159
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.221 SNIP 1.16
BFI (2008): BFI-level 1
Biocompatible Polymeric Materials Intended for Drug Delivery and Therapeutic Applications

With the advent of the controlled free radical polymerization techniques and the novel highly efficient coupling technique ("click chemistry") a number of new design principles for biomedical polymeric materials emerge. We've recently initiated a comprehensive research programme aiming at elucidating strategies for combination of biocompatible polymers in unique but amphiphilic manners. The targeted, documented biocompatible polymers like polycapro-lactone (PCL), poly(2-methoxyethyl acrylate) (PMEA) with the highest known blood compatibility, poly(methyl methacrylate) (PMMA), and the two water soluble polymers, polyethylene glycol (PEG), and poly(acrylic acid) (PAA) with good mycoadhesive properties, are all prepared by living/controlled polymerization techniques. These techniques, atom transfer radical polymerization (ATRP) and ring opening polymerization (ROP), ensure at the same time both good molecular weight control and well defined, manageable structural end groups that sets the scene for combination of the different polymer blocks. With this toolbox at hand the choice becomes to decide between all polymerization strategies or build in chemical functionalities allowing coupling of polymer blocks by "click chemistry". An all polymerization strategy would imply preparing polymers by living/controlled techniques in such a manner that one block after polymerization can be converted to a macroinitiator enabling the second block to polymerize. The coupling strategy invariably inserts a linking unit, 1,4-triazol, resulting from the catalyzed, irreversible 1,3-dipolar cycloaddition reaction between an alkyne and an azide. Thus, this strategy necessitates the proper end functionalization of the polymeric building blocks. Fortunately the 1,4-triazol unit is FDA approved already existing in formulated drugs. Examples of combinations of PMEA with PMMA or PEG will be elaborated. Similarly combinations of PCL with PAA (prepared from a protected precursor polymer) or PEG will be provided.

General information
State: Published
Organisations: Department of Chemical and Biochemical Engineering, The Danish Polymer Centre, Technical University of Denmark
Authors: Hvilsted, S. (Intern), Javakhishvili, I. (Intern), Bednarek, M. (Intern), Jankova Atanasova, K. (Intern), Pedersen, D. A. (Ekstern), Thomsen, A. D. (Intern)
Pages: 1055-1056
Publication date: 2007

Host publication information
Title of host publication: ECCE-6 Book of Abstracts
Volume: 1
Publisher: Technical University of Denmark
ISBN (Print): 978-87-91435-56-0
Main Research Area: Technical/natural sciences
Conference: European Congress of Chemical Engineering - 6 : EFCE Event Number 669, Copenhagen, 01/01/2007
Controlled Polymerization, Block Copolymers, Polycaprolactone, Poly(ethylene glycol), Poly(meth)acrylates
Source: orbit
Source-ID: 205469
Publication: Research - peer-review › Article in proceedings – Annual report year: 2007

Novel Polymers with a High Carboxylic Acid Loading

ABSTRACT: Click chemistry has been used to prepare a range of novel polymers with pendant carboxylic acid side groups. Four azido carboxylic acids, either mono- or difunctional and aliphatic or aromatic, have been prepared and thoroughly characterized. Extensive model reactions with 1-ethyl-4-hydroxybenzene, the simplest model for poly(4-
hydroxystyrene), and the four azido carboxylic acids have been conucted to establish the proper reaction conditions and provide an analytical frame for the corresponding polymers. Poly(4-hydroxystyrene) moieties in three different polymers—poly (4-hydroxystyrene), poly(4-hydroxystyrene-co-methyl methacrylate), and poly(4-hydroxy-styrene-b-styrene)---have been quantitatively transformed into oxypropynes by the use of either Williamson or Mitsunobu strategies and subsequently reacted with the azido carboxylic acids. Detailed differential scanning calorimetry investigations of all the polymers in general exhibit (when poly(4-hydroxystyrene) is a substantial part) significant changes in the glass-transition temperature from the polar poly(4-hydroxystyrene) (120—130 °C) to the much less polar alkyne polymers (46—60 DC). A direct correlation between the nature of the pendant groups in the derivatized polymers and the glass-transition temperature has emerged: the aromatic carboxylic acids give high glass-transition temperatures (90—120 DC), and the aliphatic carboxylic acids give lower glass-transition temperatures (50—65 DC).
The Thermodynamics and Electrochemical Performance of Polymeric Ionic Liquids Gel Composite Electrolyte

Department of Chemical and Biochemical Engineering
Period: 01/01/2017 → 31/12/2019
Number of participants: 3
Phd Student:
Shen, Peng (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Main Supervisor:
Szabo, Peter (Intern)

Design and Fabrication of Functionalized Ionic Liquid-based Polymeric Composite Membrane for CO2 Separation

Department of Chemical and Biochemical Engineering
The Danish Polymer Centre
Period: 01/11/2015 → 31/10/2018
Number of participants: 5
Phd Student:
Song, Ting (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Zhang, Suo-Jiang (Ekstern)
Zhang, Xiangping (Ekstern)
Main Supervisor:
Szabo, Peter (Intern)

Design and Fabrication of Functionalized Ionic Liquid-based Polymeric Composite Membrane for CO2 Separation

Department of Chemical and Biochemical Engineering
Period: 01/11/2015 → 31/10/2018
Number of participants: 5
Phd Student:
Song, Ting (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Zhang, Suo-Jiang (Ekstern)
Zhang, Xiangping (Ekstern)
Main Supervisor:
Szabo, Peter (Intern)
Transition metal catalysis for synthesis of green, renewable, chemical building blocks

Department of Chemistry
Period: 01/05/2015 → 30/04/2018
Number of participants: 4
Phd Student:
Larsen, Daniel Bo (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Fristrup, Peter (Intern)
Main Supervisor:
Duus, Jens Øllgaard (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Modification of polymer surfaces to enhance enzyme activity and stability

Department of Chemical and Biochemical Engineering
Period: 01/08/2014 → 31/07/2017
Number of participants: 4
Phd Student:
Hoffmann, Christian (Intern)
Supervisor:
Pinelo, Manuel (Intern)
Woodley, John (Intern)
Main Supervisor:
Daugaard, Anders Egede (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Samfinansieret - Andet
Project: PhD

A chemical approach to avoiding electromechanical instabilities in dielectric electroactive polymer films

Department of Chemical and Biochemical Engineering
Period: 01/12/2013 → 15/05/2017
Number of participants: 6
Phd Student:
A Razak, Aliff Hisyam (Intern)
Supervisor:
Szabo, Peter (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Daugaard, Anders Egede (Intern)
Carpi, Federico (Ekstern)
Sommer-Larsen, Peter (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Stipendie fra udlandet
Project: PhD

Supramolecular Polymeric Rheology

Department of Chemical and Biochemical Engineering
Period: 01/10/2013 → 14/12/2016
Number of participants: 6

Phd Student:
Shabbir, Aamir (Intern)

Supervisor:
Skov, Anne Ladegaard (Intern)

Main Supervisor:
Hassager, Ole (Intern)

Examiner:
Daugaard, Anders Egede (Intern)
Creton, Costantino (Ekstern)
Ianniruberto, Giovanni (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Marie Curie (EU-stipendium)

Relations
Publications:
Rheology of Supramolecular Polymers
Project: PhD

Microcapsules as delivery vehicles
Department of Chemical and Biochemical Engineering
Period: 15/09/2013 → 15/03/2017
Number of participants: 6

Phd Student:
Mazurek, Malgorzata Natalia (Intern)

Supervisor:
Hvilsted, Søren (Intern)

Main Supervisor:
Skov, Anne Ladegaard (Intern)

Examiner:
Daugaard, Anders Egede (Intern)
Hietala, Sami Heikki Olavi (Ekstern)
Paulsen, Andreas Lundtang (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU) Samf.
Project: PhD

Synthesis and Evaluation of Structures Lipids based Polyurethanes for Sensors, Actuators and Generators through Monte Carlo Simulation
Department of Chemical and Biochemical Engineering
Period: 15/01/2013 → 26/05/2016
Number of participants: 7

Phd Student:
Zakaria, Shamsul Bin (Intern)

Supervisor:
Daugaard, Anders Egede (Intern)
Gernaey, Krist V. (Intern)

Main Supervisor:
Skov, Anne Ladegaard (Intern)

Examiner:
Daugaard, Anders Egede (Intern)
Jager, Edwin Willem Harm (Ekstern)
Sarban, Rahimullah (Intern)
Financing sources
Source: Internal funding (public)
Name of research programme: Stipendie fra udlandet

Relations
Publications:
Electrical Breakdown and Mechanical Ageing in Dielectric Elastomers
Project: PhD

Novel clay/nanocellulose biocomposite films and coatings in the context of packaging applications
Department of Chemical and Biochemical Engineering
Period: 01/10/2012 → 20/09/2016
Number of participants: 7
Phd Student:
Trifol Guzman, Jon (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Hassager, Ole (Intern)
Main Supervisor:
Szabo, Peter (Intern)
Examiner:
Skov, Anne Ladegaard (Intern)
Niska, A. Kristiina Oksman (Ekstern)
Rojas, Orlando (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Marie Curie (EU-stipendium)

Relations
Publications:
Hybrid nanocellulose/nanoclay composites for food packaging applications
Project: PhD

Monolithic structures and their influence on electromechanical breakdown phenomena
Department of Chemical and Biochemical Engineering
Period: 01/08/2012 → 03/06/2015
Number of participants: 6
Phd Student:
Hassouneh, Suzan Sager (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Szabo, Peter (Intern)
Jager, Edwin Willem Harm (Ekstern)
Sommer-Larsen, Peter (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: 1/3 DTU-stip, 2/3 FUR/andet
Project: PhD

Synthesis and development of novel coating components for exterior wood applications based on sustainable resources
Department of Chemical and Biochemical Engineering
Period: 01/08/2012 → 22/02/2016
Number of participants: 6
Phd Student:
Nguyen, Hiep Dinh (Intern)
Supervisor:
Hvilsted, Søren (Intern)
Main Supervisor:
Daugaard, Anders Egede (Intern)
Examiner:
Skov, Anne Ladegaard (Intern)
Johansson, Mats (Ekstern)
Paulsen, Andreas Lundtang (Intern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: 1/3 DTU-stip, 2/3 FUR/andet

**Relations**
Publications:
Bio-based alkyds by direct enzymatic bulk polymerization

**Development of new materials for dielectric electroactive polymers as actuators and generators**
Department of Chemical and Biochemical Engineering
Period: 15/08/2011 → 26/11/2014
Number of participants: 7
Phd Student:
Madsen, Frederikke Bahrt (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Hvilsted, Søren (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Kiil, Søren (Intern)
Brook, Michael Adrian (Ekstern)
Graz, Ingrid Maria (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU) Samf.
Project: PhD

**Development of stimuli-responsive polymer network**
Department of Chemical and Biochemical Engineering
Period: 01/08/2011 → 17/12/2014
Number of participants: 6
Phd Student:
Ma, Baoguang (Intern)
Supervisor:
Hvilsted, Søren (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Daugaard, Anders Egede (Intern)
Hietala, Sami Heikki Olavi (Ekstern)
Paulsen, Andreas Lunding (Intern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Eksternt finansieret virksomhed
Project: PhD

**Large Scale Processing of dielectric electro active polymers**
Department of Chemical and Biochemical Engineering
Period: 01/08/2011 → 30/09/2014
Number of participants: 7
Phd Student:
Vudayagiri, Sindhu (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Kjørboe, Lars Georg (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Szabo, Peter (Intern)
Shea, Herbert R. (Ekstern)
Sommer-Larsen, Peter (Intern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Offentlig finansiering
Project: PhD

**Mechanical characterization methods for dielectric electroactive polymers**
Department of Chemical and Biochemical Engineering
Period: 01/08/2011 → 26/11/2014
Number of participants: 6
Phd Student:
Goswami, Kaustav (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
von Solms, Nicolas (Intern)
Benslimane, Mohamed Yahia (Ekstern)
Opris, Dorina (Ekstern)

**Financing sources**
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU) Samf.
Project: PhD

**Stimuli-Adaptable Materials**
Department of Chemical and Biochemical Engineering
Period: 01/05/2009 → 21/05/2013
Number of participants: 7
Phd Student:
Frankær, Sarah Maria Grundahl (Intern)
Supervisor:
Daugaard, Anders Egede (Intern)
Kiil, Søren (Intern)
Main Supervisor:
Skov, Anne Ladegaard (Intern)
Examiner:
Hvilsted, Søren (Intern)
Hansen, Kristoffer Karsten (Intern)
**Self-Healing anticorrosive coatings**

Department of Chemical and Biochemical Engineering  
Period: 01/01/2009 → 20/08/2012  
Number of participants: 7  
Phd Student: Nesterova, Tatyana (Intern)  
Supervisor: Dam-Johansen, Kim (Intern) Pedersen, Lars Thorslund (Intern)  
Main Supervisor: Kiil, Søren (Intern)  
Examiner: Daugaard, Anders Egede (Intern) Rasmussen, Søren Nyborg (Ekstern) Zwaag, Sybrand van der (Ekstern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: Institut stipendie (DTU)  
Project: PhD

**Micro-sensor based on Click Chemistry**

Department of Chemical and Biochemical Engineering  
Period: 01/03/2006 → 27/05/2009  
Number of participants: 5  
Phd Student: Daugaard, Anders Egede (Intern)  
Main Supervisor: Hvilsted, Søren (Intern)  
Examiner: Woodley, John (Intern) Binder, Wolfgang H. (Ekstern) Hult, Anders (Ekstern)

**Financing sources**  
Source: Internal funding (public)  
Name of research programme: 1/3 FUU, 1/3 inst 1/3 Andet  
Project: PhD

**Activities:**

**Enzymatisk polymerisation anvendt til fremstilling af biobaserede materialer**  
Period: 26 Oct 2016  
Anders Egede Daugaard (Invited speaker)  
Department of Chemical and Biochemical Engineering  
The Danish Polymer Centre

**Description**  
Foredrag for Dansk Lak og Farvekemikeres Forening

Documents:
**Abstract AED DLFF - short**

**Related external organisation**

**Unknown external organisation**
Activity: Talks and presentations › Conference presentations

**Enzymatisk polymerisation anvendt til fremstilling af biobaserede materialer**
Anders Egede Daugaard (Invited speaker)
Department of Chemical and Biochemical Engineering
The Danish Polymer Centre

**Description**
Foredrag for Dansk Lak og Farvekemikeres Forening

**Documents:**
Abstract AED DLFF - short

**Related external organisation**

**Unknown external organisation**
Activity: Talks and presentations › Conference presentations

**4th STIPOMAT Conference**
Period: 21 Sep 2008 → 24 Sep 2008
Anders Egede Daugaard (Participant)
Department of Chemical and Biochemical Engineering
The Danish Polymer Centre

**Description**
Talk about "Functionalized conducting Polymers for Cell Processing" presented at 4th STIPOMAT Conference

Place: Lacanau, France

**Related event**

**4th STIPOMAT Conference**
21/09/2008 → 29/09/2008
Lacanau, France
Activity: Attending an event › Participating in or organising a conference