Book of Abstracts

11th International Workshop on Silicone Polymers 2017

2-6 July 2017, Snekkersten, Denmark
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1 Welcome to the International Workshop on Silicone Polymers

It is a pleasure for us to welcome you to the 11th International Workshop on Silicone Polymers 2017 in Snekkersten, Denmark. The workshop is hosted by the Danish Polymer Centre, DTU, in the conference facilities of Comwell Borupgaard, Snekkersten, which is situated 30 minutes north of Copenhagen with public transportation and close to the scenic historic site of Kronborg Castle which has been immortalized by being the settings of Shakespeare’s Hamlet. There are many mysteries surrounding Shakespeare but after the social tour we will have expanded our knowledge on this topic.

And with respect to the possibilities and scientific mysteries of silicone polymers, we are very happy to announce a diverse and interesting programme for the workshop with contributions from a wide range of universities and companies across the World. Our 8 invited speakers will hopefully open up for new perspectives of silicone polymers with respect to synthesis, fabrication, and products thereof. With many interesting talks and posters we are sure that we will all be highly enlightened after the conference.

The schedule offers plenty of opportunities for extensive discussions, to establish new contacts and to strengthen existing relationships after the oral presentations, during the poster sessions or at the social events such as running and ocean swimming for the Vikings-wannabe’s. Last but not least we also want to acknowledge the generous sponsorships from companies worldwide.

We are looking very much forward to some enjoyable days in good company.

Sincerely,

The Organizing Committee

Anders Egede Daugaard
Associate Professor, DTU

Søren Hvilsted
Professor, DTU, IDA Polymer

Anne Ladegaard Skov
Head of Danish Polymer Centre, DTU
2 General information

Transportation from Copenhagen Airport in Kastrup to Comwell Borupgaard

The access from the Airport to the venue, Comwell Borupgaard in Snekkersten, is in principle easy by train directly from the arrival terminal. Purchase a ticket bound for Snekkersten (Øresundstog, return ticket is recommended) at the DSB ticket booth in the terminal – departures are frequent (at least 3 trains per hour).

Unfortunately the trains stop at the Rungsted Kyst station due to track maintenance and improvement over the summer. At Rungsted Kyst you need to transfer to a bus (Togbus, the train ticket is still valid for the bus). Any bus color coded red, blue or orange will take you to Snekkersten. From the bus stop there is approx. 400 m to Comwell Borupgaard.

Conference venue

The conference venue is Comwell Borupgaard, Nørrevej 80, 3070 Snekkersten. All lectures will take place in our main conference room, where the poster session will also take place. All conference delegates will have free access to the open wireless network available at the hotel.

Coffee, Lunch and dinner

During the conference there will be coffee outside the conference room and all meals will be taken in the restaurant (water is included in meals). If you would like to have other drinks together with your meals, there will be a possibility to buy them. During the conference the hotel bar will also be available for your
convenience.
The conference dinner will take place in the old timber frame building on Wednesday, where we will meet outside at 19:00 (weather permitting).

Registration and registration desk
On Sunday the registration desk will be placed in the reception of the hotel from 15-17. For later registrations the registration desk will be outside the conference room during the conference, where it will be open for registration during the breaks. Please ensure that you register for social activities and the trip to Kronborg, if you want to participate.

Posters
Posters will be displayed in the main conference room, where we will have the poster session on Tuesday from 14:30-17. Please mount your posters on arrival or at the latest before the poster session. You are welcome to leave your posters mounted for the whole conference. During the poster session, drinks will be served (included in the conference). All posters should be mounted as soon as possible on Sunday and removed on Thursday morning or before you leave.

Exhibition
We are happy to host 2 companies for the exhibition during the conference. They will have stands close to the Coffee/break area. Please take your time to visit them.

Conference awards
Thanks to our sponsors, there will be awards for posters as well as an award for the best young presenter. The winner will be announced at the closing ceremony on Thursday the 6th.

3 Social events
We have arranged a trip to Kronborg Castle in Elsinor on Wednesday the 5th of July with a guided tour of the castle. For more information on Kronborg, see their website. We will leave by bus from the conference venue at 14:25 (please be on time) and return after the excursion for the conference dinner.

Sports and other activities:
Remember your swimming and running gear if you would like to engage in some of the social activities coordinated. The spa facilities are open and can be accessed for free. The ocean is also nearby. There will also be guided runs in the morning:

Running trip 1: Experience the Danish coastline
The route is 4.8 km long which starts and finishes at the conference venue. For most of the running time the participants will be enjoying delightful views from the coastal promenade and a gentle morning breeze coming from the Baltic sea. Additionally there will be plenty of opportunities to dive into the refreshing
local sea waters. The coast is particularly charming in this area.

Running trip 2: Experience the Danish forests

This charming 5.2 km route starts as finishes at the conference venue. After getting warmed up passing by an inhabited area we will quickly immerse into the "wild" of Danish forests. The mysticism created by a combination of beeches, ponds and narrow streams will not let you forget about this running trail. On the way back there will be one short stop for a morning dive.

Competition - ISPO champion of "Kongespil":

During the conference a special competition in the nordic game "Kongespil" will be arranged. Please sign up for the competition on arrival - you only need to be 3 team members to participate. There will be "free practice" on Monday evening and instructions in the rules. The actual competition will take place Tuesday evening. There will be refreshments for the participants (included in the conference fee).

May the best team win!
4 Program

Sunday

Arrival

15-18 Registration
Get-together reception
18:30 Dinner

Monday

<table>
<thead>
<tr>
<th>Morning</th>
<th>Breakfast</th>
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<tbody>
<tr>
<td>Conference opening</td>
<td>8:50</td>
</tr>
<tr>
<td>PL1: Brook</td>
<td>9:10</td>
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<tr>
<td>OL1: Kongsfelt</td>
<td>10:00</td>
</tr>
<tr>
<td>Coffee</td>
<td>10:20</td>
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<tr>
<td>OL2: Langhals</td>
<td>11:00</td>
</tr>
<tr>
<td>OL3: Pisula</td>
<td>11:20</td>
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<tr>
<td>OL4: Larribe</td>
<td>11:40</td>
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<tr>
<td>12:10-13:20 Lunch</td>
<td></td>
</tr>
<tr>
<td>IL1: Vovelle</td>
<td>13:20</td>
</tr>
<tr>
<td>OL5: Unno</td>
<td>13:50</td>
</tr>
<tr>
<td>OL6: Looze</td>
<td>14:10</td>
</tr>
<tr>
<td>Coffee</td>
<td>14:30</td>
</tr>
<tr>
<td>IL2: Graz</td>
<td>15:10</td>
</tr>
<tr>
<td>OL7: Güney</td>
<td>15:40</td>
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<tr>
<td>OL8: Katsoulis</td>
<td>16:00</td>
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<tr>
<td>18:30 Dinner</td>
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<tr>
<td>Evening Kongespil practice</td>
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## Tuesday

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>Morning</td>
<td>Breakfast</td>
</tr>
<tr>
<td>9:00-11:50</td>
<td>IL3: Marciniec 9:00&lt;br&gt;OL9: Jégou 9:30&lt;br&gt;OL10: Pouget 9:50</td>
</tr>
<tr>
<td></td>
<td>Coffee 10:10</td>
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<tr>
<td>12:00-13:20</td>
<td>Lunch</td>
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<tr>
<td></td>
<td>Coffee 14:30</td>
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<tr>
<td>15-17</td>
<td>Poster session&lt;br&gt;(Snacks and refreshments)</td>
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<tr>
<td>18:00</td>
<td>Dinner</td>
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<tr>
<td>19:30</td>
<td>Kongespil</td>
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## Wednesday

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<thead>
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<th>Time</th>
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<tbody>
<tr>
<td>Morning</td>
<td>Breakfast</td>
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<tr>
<td>9:00-11:50</td>
<td>PL2: Ganachaud 9:00&lt;br&gt;OL16: Macphail 9:50</td>
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<tr>
<td></td>
<td>Coffee 10:10</td>
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<tr>
<td></td>
<td>OL17: Alentev 10:50&lt;br&gt;OL18: Bui 11:10&lt;br&gt;OL19: Madsen 11:30</td>
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<tr>
<td>12:10-13:20</td>
<td>Lunch</td>
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<tr>
<td>14:25</td>
<td>Departure for Kronborg</td>
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<tr>
<td>15:30-18</td>
<td>Visit to Kronborg</td>
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<tr>
<td>19:00</td>
<td>Conference Dinner</td>
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### Thursday

<table>
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<tr>
<th>Morning</th>
<th>Breakfast</th>
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<tbody>
<tr>
<td>IL6: Dyshelman</td>
<td>9:00</td>
</tr>
<tr>
<td>OL21: Mazurek</td>
<td>9:30</td>
</tr>
<tr>
<td>OL22: Biele</td>
<td>9:50</td>
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<tr>
<td>9:00-12:15</td>
<td>Coffee 10:10</td>
</tr>
<tr>
<td>OL23: Chen</td>
<td>10:50</td>
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<tr>
<td>OL24: Ogliani</td>
<td>11:10</td>
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<td>IL7: Saab</td>
<td>11:30</td>
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<td></td>
<td>Conference conclusion 12:00</td>
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<td></td>
<td>Prizes and perspectives 12:00</td>
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<tr>
<td>12:15-13:20</td>
<td>Lunch</td>
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<tr>
<td></td>
<td>Departure</td>
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5 Poster presentations

Liyun Yu:
Electrical breakdown phenomena of dielectric elastomers (P1)

Anna Szymańska:
Functionalization of SSBR by [bis(trihydrocarbylsilyl)amino]-substituted styrene derivatives (P2)

Valeria Chiaula:
Heterogeneous bimodal condensation elastomers: an opportunity for many applications (P3)

Alena Jurásková:
Self-healing dielectric silicone elastomers with high dielectric permittivity and good mechanical properties (P4)

Constance Robeys:
Microstructure versus mechanical properties of original silicone/thermoplastic elastomer blends (P5)

Vadim Gorodov:
PDMS containing carboxyl groups (P6)

Sevgi Gündey:
Electrochemical determination of endocrine disrupting chemical by using electrode modified with imprinted sol-gel particles (P7)

Magali Puillet:
A new class of catalysts for hydrosilylation reaction (P8)

Andreas Ziegmann:
Evaluation of the electromechanical transduction performance of silicone elastomers filled with bariumtitanates of different particle sizes (P9)

Jonas Daenicke:
Evaluation of the diffusion properties of silicone elastomers related to the crosslinking density and of the mechanical weakening due to silicone oil up-take (P10)

Claus Berner:
Investigation of various influences on the dielectric breakthrough strength of a silicone elastomer (P11)

Lucile Fauvre:
Supramolecular polydimethylsiloxanes: Towards self-healing materials (P12)

Aleksandra Chechelska:
Synthesis and characterization of poly(methylhydrosiloxane) and its copolymers (P13)

Aleksandra Chechelska:
Polysiloxane and polysiloxane-silazane networks with incorporated palladium particles (P14)

Cody Gale:
Synthetic Routes to Silicone-Modified Soybean Oil Copolymers (P15)

Nicole Amaral:
Should We Sugarcoat it? Silicone Elastomers Modified with Pullulan and Glycerol (P16)

Prateek Saxena:
Application of silicone based elastomers for manufacturing of Green Fiber Bottle (P17)

Harald von Hanstein:
Mechanical properties of silicone breast implants under compression load and its effect on the implant shape and the shell material (P18)

Malgorzata Mazurek:
Soft bottlebrush PDMS elastomers (P19)

Malgorzata Mazurek:
Magnetically Activated Microcapsules - Preparation and Characterization (P20)

Raphaël Miralet:
Efficient transition-metal catalysts for hydrosilylation using a strong donating silylene ligand (P21)

Thorbjørn Sorensen:
Modeling of energy losses in dielectric elastomers (P22)
6 Plenary lectures

PL1: Finding the cure: alternative strategies to crosslink silicone elastomers

Michael Brook; Robert Bui; Mengchen Liao; Scarlet Zhang; Ayodele Fatona; Yang Chen; Jose Moran-Mirabel
Chemistry and Chemical Biology, McMaster University

Silicones are commonly cured into elastomers through radical, moisture cure (RTV) and hydrosilylation-induced crosslinking because these are very reliable, and flexible crosslinking systems. However, each of these processes has disadvantages, particularly slow reaction rates.

We are interested in developing fast cure processes for silicones and have turned to simple organic chemistry. In addition to work already described that uses metal-free azide/alkyne click chemistry [1], and epoxide ring opening, as described by Crivello [2], it is possible to prepare elastomers using a variety of Michael additions [3], but none of these was particularly rapid.

Thiol-ene click chemistry has previously been used to cure a variety of polymers, including silicones [4]. When optimized, it was discovered cure times of less than 10 seconds are possible using UV; the reactions in blue visible light are somewhat slower; other sulfur-based reactions give similarly interesting results. For example, the preparation of dithioacetals provides an attractive route to cure, with unusual triggers for the retro reaction. The reaction of aminosilicones with aldehydes can be made to occur in less a second or two, but sometimes leads to coloured elastomers.

The presentation will outline the benefits and detriments of these organic routes to silicone elastomers and silicone/organic copolymers.

References
PL2: Supramolecular silicone elastomers: from fun to applications

François Ganachaud
INSA-Lyon, IMP, CNRS UMR 5223, 17 avenue Jean Capelle 69621 Villeurbanne

Conventional silicone elastomers are silica-(highly) filled, (lightly) crosslinked PDMS materials, that can not be reprocessed afterwards. Supramolecular chemistry allows replacing (possibly a part of) the covalent bonds by physical, reversible ones. This paper proposes to first summarizes the different studies that have been published on the literature on this field, and then to present some original work from our laboratory. In particular, materials crosslink through hydrogen bonds are available currently on the market that were implemented after a 20 years development in academia. Other physical crosslinking processes, such as based on ion-pairs, become more and more used nowadays, because they combine rather high chemical and thermal stabilities, with some reversibility achievable through competing association. I will finally particularly focus on the various properties one ought to achieve with these new types of materials, including transparency, damping, self-healing or unique stress-strain properties.
7 Invited lectures

IL1: Silicones: New materials and new performances - Discoveries to Innovations

Louis Vovelle
Elkem-Bluestar Silicones

Silicones materials are known for their high performances with amazing mechanical and physical properties. Our industry has to face new challenges for the future with an increasing demand for new performances linked to megatrends such as Transportation including urbanization and mobility, Environment protection and renewable energy, Health Care, Digital transformation with smart materials and 3D/4D printing...

These demands are very energizing for our Innovation but the complexity and the emergency of the needs question: 1. The way we develop our Innovations and the essential partnerships to gather new competences 2. The full value chain from the chemistry to the final products and the required properties. In this context, Bluestar Silicones will present examples of Innovations in partnership with Academics 1. Design of new catalysts or new systems for developing new materials either showing a better compromise between reactivity, stability or enhancing the cost/efficiency compromise 2. Development such as 3D printing for new health care devices where catalysts and kinetics are key to have the best compromise between reactivity, shaping and performances

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Hand a physicist a piece of silicone elastomer and you will be surprised what he/she comes up with. Their extreme elastic properties, similar to biological tissue such as skin or muscles, are inspiring: Not only are silicones the perfect platform for stretchable electronics mimicking the human skin, but also an excellent choice for actuators and soft robots. In this talk, I will first introduce two skin-inspired concepts of stretchable electronic skins with the ability to sense pressure, stretch and temperature. I will then show their application in soft machines before concluding with a wish list to materials developer.
II.3: Synthesis of new multifunctional silsesquioxanes and heterosilsesquioxane derivatives via TM catalyzed reactions

Bogdan Marciniec
Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89B, 61-614 Poznan, Poland Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89C, 61-614 Poznan, Poland Fax : +48 61 8291 987

Functionalized polyhedral silsesquioxanes of the general formula (RSiO3/2)n , known for their inorganic - organic cores of defined architecture with organic moieties attached to it, have become representatives of hybrid compounds that meet the needs of science and industry. Many of their physical and chemical properties, e.g. low dielectric constant and very good thermal stability, allow their application in many branches of chemistry, material or even medicinal science. [1] Within the silsesquioxide family, cubic T8 cages play a key role, also in a not completely condensed form, allowing introduction of two or three functional groups. Just over a decade ago, a new class of silsesquioxyl compounds, i.e. double-decker silsesquioxane (DDSQ) was presented. These compounds may have an open (T12) or closed (T10) structure with either four or two reactive groups, respectively, and their chemistry is related with the type and number of functional groups. [2]

In this lecture, our recent results on the synthesis of new di-, tri- and tetrafunctional substituted silsesquioxanes of both cubic and double-decker architecture are presented. These silsesquioxanes are subjected to TM catalyzed processes, depending on the type of functional groups attached to Si-O-Si core, including hydrosilylation, metathesis or silylative coupling reactions. These processes enable efficient and selective synthesis of new types of molecular silsesquioxane based compounds to be used as models in their further application in formation of co-oligomeric hybrid systems or polymeric matrixes.[3]. The co-oligomers show interesting thermal properties and may be attractive materials with a great application potential.

Acknowledgment: The author gratefully acknowledges the financial support from the National Centre for Research and Development in Poland - PBS3/A1/16/2015, National Science Centre (Poland) - DEC-2012/05/D/ST5/03348 and the European Regional Development Fund, Operational Programme Innovative Economy, 2007-2013, Project No. UDA-POIG.01.03.01-30-173/09.

References
Combining the highly hydrophobic silicone backbone with highly polar amino acid functionalities renders novel products with interesting properties: the highly polar charged betaine structures of the amino acid moieties are capable to interact strongly with each other and also with polar surfaces, leading to various potential applications. Advantageously, many amino acids are available on technical scale at a low price. Nevertheless, to date there are only few investigations[1-3] regarding this class of compounds. We developed simple procedures[4] to provide various amino acid modified silicones starting mainly from lysine and glutamic acid. Depending on the structure, the resulting products improve the softening and rewetting properties of textiles, and show enormous thickening effects of water. Furthermore, some of the materials are super-absorbents of water and show controlled release of active agents especially in an aqueous environment.

References
IL5: Electrophilic Substitution on Phenylsilsesquioxanes

Dept of Materials Science and Engineering, Chemistry and Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, U.S.A.

Phenylsilsesquioxanes, \([\text{PhSiO}_{1.5}]_{8,10,12}\) undergo a surprising number of novel electrophilic reactions that cannot be directly correlated with traditional concepts of electrophilic substitution at functionalized benzene. Although the T8, T10 and T12 \([-\text{SiO}_{1.5}]_{x}\) cages exhibit strongly electron withdrawing character equal to a traditional -CF3 group the phenyl rings can undergo electrophilic substitution at the ortho, meta or para positions depending on the reactants. Thus, nitration, sulfonylation or acetylation give traditional meta substitution, whereas bromination goes almost exclusively ortho and iodination goes almost exclusively para providing diverse starting materials for a wide variety of hybrid materials applications. In this study we examine the mechanisms involved that strongly suggest electronic effects not anticipated by the simple structures. Theoretical modeling studies combined with extensive studies on the effects of electrophilic substitution on the title cage compounds, their photonic properties in particular indicate that the cage structures themselves strongly influence the electronic character of the transition state in the noted electrophilic reactions. A detailed understanding of the processes that transpire offers a facile new route to two faced (Janus) cages of potentially significant value for multiple fields of study.

References
3. M. Bahrami, X. Zhang, M. Ehsani, Y. Jahani, R.M. Laine, \([\text{PhSiO}_{1.5}]_{8,10,12}\) as nanoreactors for non-enzymatic introduction of ortho, meta or para-hydroxyl groups to aromatic molecules, Dalton Trans. In press

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ACEO is revolutionizing the world of additive manufacturing by introducing the world’s first real elastomer which can be 3D printed. The drop on demand process enables freedom in design and accuracy. Therefore proven silicone experts developed not only the material, but also software and hardware opening up new opportunities for various industries such as health care, automotive, electronics or even lifestyle goods only to name a few.

ACEO is a registered trademark of Wacker Chemie AG, a leading supplier of silicones. ACEO is offering a worldwide service for 3D printed silicone parts out of its site in Burghausen, Germany. This is rounded up by development services for design and material; whereas in the Open Print Lab, designers and customers can experience the technology under the guidance of the ACEO expert team.

Visit www.aceo3d.com to find out more.

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IL7: A Multi-scale Experimental and Computational Approach to Studying Network Dynamics in Complex Polysiloxane Elastomers

Lawrence Livermore Natl. Laboratory. 7000 East Ave. L-231, Livermore, CA 94550, US

Linear polysiloxanes show remarkable and often highly ideal behavior from a polymer physics standpoint. The polydimethylsiloxane (PDMS) chain is extremely flexible and translationally mobile. PDMS has a large molar volume and the polymer chains can coil and uncoil very freely over ambient temperatures and reasonable timescales of study. As such, linear PDMS is often the ‘polymer of choice’ for magnetic resonance based polymer physics studies into the fundamentals of chain dynamics and large scale cooperative processes in polymer melts. However, polysiloxanes are often employed in application not as simple linear polymers but as complex, hierarchical network composites.
These complex and often ill-defined polymer networks present both an experimental/computational challenge and an opportunity to develop our knowledge and skillset in polymer network theory. At LLNL we are invested in making accurate assessments and predictions of polysiloxane network based materials performance and lifetimes over a broad range of environmental conditions, therefore we are actively studying and modeling the relationships between underlying network architecture, dynamics, physical properties, materials performance, stability and lifetime. In this lecture we will discuss a combined multilevel experimental & computational approach towards understanding structure property relationships in polysiloxane networks through; experimental solid state NMR, thermal, and mechanical analysis - in conjunction with network and finite element modeling & simulation.
This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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8 Oral lectures

OL1: Strong and safe adhesion of silicone polymers on metal parts utilizing covalently attached polymer brushes

Mikkel Kongsfelt; Stefan Urth Nielsen
RadiSurf ApS

Due to their versatility, unique abilities and availability silicone elastomers offer an almost endless range of applications in various business segments. Of especial importance, due to their low reactivity in biological systems, are the food and medico applications. However only very few viable solutions for lasting adhesion between silicone elastomers and other materials exist today. RadiSurf are working to commercialize a novel and innovative strategy for safe and clean adhesion between metal and polymer materials based on polymer brushes. We are basically growing nanometer thin covalently attached porous polymer structures on metal surfaces. Structures, that are capable of making a stable and strong chemical bridge between the metal and the polymer. Due to the covalent attachment, the low thickness and chemical stability of the brushes they provide a very safe way of achieving strong adhesion compared to traditional primers and adhesives. We are developing new technologies for industrial scale application of polymer brushes for adhesion applications within all types of polymers, including silicone elastomers.

We will present our strategy and results for strong adhesion of silicone polymers on metal surfaces. Utilizing a 50 nanometer coating of polymer brushes, chemically bonded to metal, we are able to obtain full cohesion of silicone elastomers and other polymers on most metal parts. With an adhesion interface of only 50 nanometer, our solution provides a safe and completely tight interface for use in any type of industry, but with especially high value in food contact systems and medical device products.
OL2: Characterisation of Polymers by Means of Fluorescence Decay and Other Optical Methods

Heinz Langhals
Department of Chemistry, LMU University of Munich, Butenandtstr. 13, D-81377 Munich, Germany

The mobility of chain segments, the interaction with plasticizers and other rheology-controlling additives with macromolecular structures control even macroscopic properties of polymers. Detailed knowledge of such microscopic effects is helpful for the further development of polymeric materials, however, the micro characterisation of individual polymers remains a challenge where optical methods are attractive because easy and precise measurements. Light scattering of polymeric samples may be an obstacle, but could be overcome by the application of fluorescence. Thus, molecular interactions in macromolecular materials were studied with various optical methods where the auto fluorescence allowed a fingerprint-like characterisation of individual materials and the fluorescence lifetime. Solvatochromic fluorescent probes were applied for the characterisation of polar properties of polymers where generally, the direct solvent shell proved very thin so that a two-dimensional approach seems to be most appropriate resulting in novel aspects for the theoretical treatment of the behaviour of polymers. A universal probe for the characterisation of polymers would bring about a further progress; we found an appreciable auto fluorescence of additive pyrogenic silica widely applied for polymers exhibiting an considerable sensitivity concerning the covering medium. Basic theory of the effect was treated on the basis of the theory of light emission. Novel insights were possible with respect to the unique properties of silicones and the immiscibility of different polymers.

References

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OL3: Impact of amorphous synthetic silica on properties of silicone elastomers

Wojciech Pisula
Evonik Resource Efficiency GmbH, Rodenbacher Chaussee 4, 63457 Hanau (Wolfgang), Germany

The use of fumed silica as a reinforcing component in silicone elastomers allows for lasting improvements in mechanical properties such as tensile strength, elongation at break, and tear resistance. Fumed silica also helps control the temperature dependency of the mechanical properties. The range of the improvements of the above-mentioned properties depends on the type of silicone polymer used as well on the silica grade and its concentration. On the other hand, besides fumed oxides, precipitated silica leads to a low compression set of the final silicone products.

Silicone elastomers reinforced with fumed silica can be highly transparent allowing further pigmentation to almost any color. The transparency of such formulations is controlled by the size of the primary particles of the silica aggregates and the refractive indexes of the polymer and the filler. For this reason, certain types of fumed silica with high specific surface area are suitable for highly transparent silicone systems.

In this presentation the relationship between the specific surface area of fumed silica and mechanical as well as optical properties of silicone elastomers is discussed. Furthermore, it is shown how the nature of the silica surface when tuned from hydrophilic to hydrophobic is affecting its behavior in the silicone elastomer. Besides using purely hydrocarbonic silanes, surface modification with functional groups can be done to initiate a specific interaction between the silica and the polymer network. Finally, the mechanism of other metal oxides such as titanium dioxide to improve heat stabilization of the silicones will be discussed.

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OL4: Silicone foams from emulsions
Gabriel Larribe; François Ganachaud; Etienne Fleury
INSA-Lyon, IMP, CNRS UMR 5223, 17 avenue Jean Capelle 69621 Villeurbanne

Cellular materials are widely used in applications such as thermal and sound insulations, absorbent for liquids and low density foams. Solid foams are materials containing gaseous voids called cells, surrounded by a dense matrix. They differ in their composition, cell morphology (open or closed porosity) and physical properties. In the closed-cell materials, the voids are isolated from each other and the cavities are surrounded by a continuous wall polymer; whereas, in open-cell materials, bridges between cells allow gas or liquid diffusion. Open foams are widely seen in Nature, for example in cork, wood, sponges and corals.

Recently cellular synthetic materials were developed through chemical or physical foaming. The control of cell size and morphology is difficult to achieve with these techniques, e.g. to generate totally interconnected structures. The approach of using highly concentrated emulsions (with a fraction of at least 70% water) to prepare controlled microcellular polymers and 100% interconnected porosity, represents an attractive alternative for many applications. [1] The materials thus obtained, known as polyHIPE (High Internal Phase Emulsion), are of great interest for academic and industrial researchers, because of their easy preparation and their high application potential. In particular, Grosse et al. [2] showed that it is possible to get silicone foams crosslinked by hydrosilylation, starting from highly concentrated water-in-silicone emulsions. Using such technique, we aim at developing silicone foam elastomers, which exhibit low flammability and good mechanical properties as potential candidates for sound insulation in buildings. Foams with good mechanical properties were obtained in a simple and fast way, especially, at low densities (of 0.20) and narrow cells diameters (around 90 $\mu$m).

References

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OL5: New Generation Janus Cube

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In the field of material science, polyhedral oligomeric silsesquioxanes (POSS) have been especially attracted attention [1]. Among them, cage octasilsesquioxane or T8 is nano-scale organic/inorganic hybrid molecules, with an inorganic core and eight organic substitutions in a single molecule.

Last year, we reported the synthesis and structure determination of Janus cube that is a cage octasilsesquioxane possessing two different substituents on the opposite faces [2]. As an extension of this work, here we will report the synthesis and structures of novel Janus cubes. One (2nd gen.) is that with reactive substituents. Another (3rd gen.) is that with larger cavity. Different synthetic methods from previous Janus cube and structures will be described.

References
OL6: A new approach to characterize the micro-mechanical properties of complex polymers

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Polymeric materials are often engineered to have specific mechanical performance for certain applications. Therefore a wide variety of different mechanical properties can be observed in such materials. When rationally designing a polymeric material, understanding the mechanical behaviour of the end product is often considered important. Also structural factors like cross-linking and molecular orientation can influence the mechanical properties.

Although the global mechanical characterization of polymers is well established, the local characterization of (very) soft materials is not, as with existing instruments this is challenging to perform. In this presentation, we describe a new experimental method to derive the local micro-mechanical properties of soft materials in a non-destructive way with great accuracy and precision. The method involves a novel nano-indentation instrument that uses fiber-optical interferometry.

Both load- and displacement-controlled experiments can be performed with this novel instrument, enabling a wide range of mechanical tests. Possibilities range from quasi-static experiments to derive classical elastic modulus values, to step response tests (e.g. creep, stress-relaxation), dynamic mechanical analysis (DMA) and constant strain rate tests (i.e. epsilon-dot method) to investigate material viscoelastic behaviour.

The method proposed in this study provides a unique framework to characterise local mechanical properties of complex polymers and thin films, providing a relevant enabling technology for most researchers involved in polymer science.

Applications and data results of the instrument will be presented, compared and discussed.
OL7: Synthesis and Characterization of a Sol-Gel Derived Organic-silica hybrids Containing Nanoparticles

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Typical sol-gel derived organic-silica hybrids exhibit a combination of organic and inorganic components on a molecular scale. In contrast to conventional polymers, the formation of covalently bonded hybrid organic inorganic polymeric materials requires the presence of functionalized reactive precursors. Chemical interaction between organo-functional silane with amphiphilic polyether diols or polyether diamines give rise to transparent, rubber-like ureasilicate/urethanesil xerogels [1]. Hybrid organic-inorganic hybrids containing uniform distributions of metal nanoparticles have been prepared by mixing a preformed nanoparticle colloid with the precursors of an ureasilicate, prior to the sol-gel transition. These hybrids possess not only high optical quality and optical features dictated by the size and shape of the nanoparticle dopants but also a high degree of flexibility, which can largely enhance the range of applications in practical devices.

In this study, hybrid materials that consist of reticulated siliceous backbone covalently bonded to polyether-based segments by urea (-NHCONH-) linkages, so-called ureasilicates, were prepared. The aim of present work is to study the steady-state photoluminescence behavior of ureasilicates doped with metal nanoparticles stabilized by silica shells. Preliminary results by low temperature time resolved fluorescence measurements indicate the existence of energy transfer from the ureasilicate emitting centers to the nanoparticles.

References

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OL8: Hybrid Materials based on Functional Metallosiloxane Oligomers and PDMS as Polymer Matrix

Dimi Katsoulis; A. Muzafarov[1,2]; N. Tebeneva[2]; A. Tarasenkov[2]; I. Meshkov[1,2]

Metallosiloxane hybrid network materials were prepared via condensation reactions of metal-siloxane alkoxy monomers with functional PDMS and additional coupling agents including hyperbranched polyethoxysiloxanes [1, 2]. The processes were catalyzed by the metallosiloxane oligomers. Due to good solubility of all reagents in organic solvents and controllable chemistry for network formation we were able to tune the hybrid material properties to quite wide extent by changing the mixing ratio of components, the degree of polymerization and functionality of the PDMS segments and the nature of the metallic oligomer. During the presentation we will discuss examples of hybrid networks including their cured forms as elastic coatings and free-standing films.

References

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OL9: Influence of airtight environment on the mechanical and network properties of room temperature vulcanizing silicones

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This work is part of a study on the influence of sealed conditions on the degradation of room temperature vulcanizing (RTV) silicone elastomer properties. Those materials are usually used for their impermeability in molding, electrical and stuffing applications. Here, two components polycondensation RTVs cross-linked by metal catalysis have been focused on because of the high reliability of the reaction. However, the use of these materials in an airtight environment is limited by the production of condensation by-products, leading to a faster aging of the polymer network by a so-called "reversion" mechanism[1].

First, several commercial crosslinking systems based on organotin compounds have been studied in open and closed environments, in order to compare their reactivity and the effect of the sealed conditions on the structure of the final polymer network. Mechanical and chemical characterizations have been carried out on the final elastomers and compared to those prepared with a Sn / TEOS (tetraethoxysilane) reference system. In a second phase, we performed thermal aging tests in sealed conditions[2]. These have shown that the tin-based materials are quickly damaged compared to the open-to-air conditions. Therefore, further work will focus on the development of new crosslinking systems by modifying the nature of the metal catalysts in order to reduce the effect of the sealed conditions on RTV materials.

References

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OL10: Towards the synthesis and use of chromium free acrylate functionalized silicone polymers

Emmanuel Pouget; Christian Maliverney, Perrine Theil
Bluestar Silicones

Silicone acrylates are a well-known class of functionalized silicone polymers. They are more particularly used in UV release coating applications where the high reactivity of acrylates is highly appreciated. The combination of this high reactivity with the versatility of silicone chemistry allows the synthesis of a wide range of well architectured polymers showing very different chemical and physical properties.

One synthesis of such silicone acrylates consists in the opening of epoxy functionalized silicones with acrylic acid which gives an alcohol and an acrylate functions. Chromium (III) based catalyst are generally used for this reaction. These catalysts have the advantages to give good selectivity and kinetics but they stay in the reaction medium at the end of the synthesis.

Due to the high toxicity of Cr(VI) species that can be formed after ageing of the products, a study was carried out to avoid the use of chromium based catalysts. After a wide screening of different types of catalysts, a new family was discovered leading to greener polymers with a very good selectivity and reactivity. Moreover, no side reactions were observed. After discussing the results concerning the reaction we will present the final polymer properties and the associated UV release coatings performances.

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OL11: Adhesion testing and FEM analysis of soft silicone gaskets on titanium cores for an improved implant-skin interaction

Mark Holm Olsen; Peter Sommer-Larsen; Anna Svensson
Danish Technological Institute

A key focus for developing new implants is to improve the adhesive interface between the skin and the implant [1]. We develop implants with silicone gaskets around a titanium core. The soft silicone creates a cushion effect between the Ti and the soft skin (E~100 kPa [2]). We have performed a series of tensile adhesion experiments on a prototype implant with two different kind of surface modifications applied to the titanium: a polymer brush [3] and a commercial primer. This is done to ensure adequate adhesion between the silicone gasket and the titanium core for its use in prolonged implant devices. We have used a custom setup where we pull the Ti core from the silicone gasket. We analyze the test geometry in comparison to tensile mechanical properties of the materials used and common adhesion testing geometries. Initial fracturing forces are similar for our surface modifications compared to the Nusil adhesion primer MED1-161. The ultimate tension increases significantly when utilizing an improved polymer brush coating. We tested the soft Nusil MED4-4420 silicone (Shore A17) and the harder Nusil MED 6215 silicone (Shore A45). Additional silicone materials will be reported. We observed a higher adhesion force for the soft silicone and a cohesive fracture/failure/split mechanism for both silicones demonstrating excellent adhesion between the silicones and the Ti substrate. We present FEM modelling of a disc shaped silicone gasket. In conclusion, avoiding sharp corners and using a silicone-implant with mechanical properties similar to the skin minimizes adhesive stress along the skin-implant interface.

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Introducing of heteroatoms in composition of hyperbranched carbosilane and organosiloxane systems increases their affinity to the metal ions and metal surfaces. In our presentation nitrogen containing siloxanes and sulfur containing carbosilanes synthesis will be considered. Two different synthetic strategies were used for their preparation. Hyperbranched polyaminopropyl- and polyethylenediaminopropyl(ethoxy)siloxanes were synthesized via corresponding alkoxysodium salts which were preliminary synthesized by Rebrovs’ approach [1, 2]. Affinity of the hyperbranched polyaminoalkoxy siloxanes (HPAAS) to the silver salt allowed us to load HPAAS by silver nanoparticles after reduction of silver ions. Sulfur containing carbosilane systems were synthesized by thiolation of typical hyperbrached polyallylcarbosilane polymer [3, 4] using thiols of different structures, which supply different crowding of core molecules. The loading of the thiolmodified hyperbranched carbosilane (TMHCS) by copper ions with following reduction resulted in generation of cupper nanoparticles. High affinity of TMHCS to the iron microparticles allowed us to use it as a media of magnetic fluids [5]. Thus, both organosilicon hyperbranched systems containing heteroatoms were demonstrated as quite effective matrixes for the molecular nanocomposites preparation.

References


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OL13: Sequential Functionalization of a Natural Cross-linker Leads to Designer Silicone Networks

Scott Laengert; A. Schneider; E. Lovinger; Y. Chen; M.A. Brook
McMaster University

Silicone polymers, or polysiloxanes, are used in a wide variety of practical applications including medical implants, industrial sealants, and electronic insulators. Silicones can be produced in various forms, such as oils, gels, elastomers, hard plastics, and foams, but achieving precision control of network structures is challenging, since functional groups introduced in industrial processing are often randomly distributed along the silicone backbone.

We have developed a system for the construction of precise silicone networks using the natural product eugenol, an extract of cloves and other plants, by taking advantage of its triple functionality in a selective and sequential manner.[1] The boron-catalyzed Piers-Rubinsztajn reaction, using H-terminated silicones to create Si-O-C bonds, reacts fastest with the phenol group and slower with the methoxy group.[2] By adding a single equivalent amount of H-terminated silicone, the reaction at the phenol group takes place selectively, and subsequent addition of a second portion leads to reaction of the methoxy group. Adding a platinum catalyst and a third equivalent of Si-H leads to a hydrosilylation reaction of the silicone with the allyl group and the creation of an Si-C bond.[3] Remarkably, these two catalysts do not interfere with each other, and these three reactions can therefore be performed in any order, in the same reaction vessel, and without the need for workup of any kind. The result is that a variety of H-terminated polysiloxanes can be easily used to form chain extended polymers, elastomers, or foams in which the morphology of the material and its constituent parts can be manipulated at will.

References

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Cyclic azaasilanes have been synthesized for the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles, nanocrystals, mesoporous materials and substrates. Cyclic azaasilanes contain cryptic amine functionality that can perform a coupling reaction with functional molecules after the surface-initiated ring-opening reaction, allowing for a one-pot self-assembly route on nanostructures. Activated silanes are blends of cyclic azaasilanes with conventional silanes that provide high-speed reactivity induced by surfaces, unlike conventional silanes that require moisture for initiation. In epoxy resin systems, activated silanes with amine functionality give the benefits of moisture-free deposition, high speed reactivity, adhesion promotion, and high bond strengths between substrates. The kinetics and mechanism of cure, as well as mechanical bond strength between a variety of substrates will be investigated for a series of activated silane formulations.
Polydimethylsiloxane (PDMS) elastomers show outstanding resistances to high and low temperatures, but on the other hand they swell in a wide range of industrially used fluids and oils.[1] Fluorosilicones (FS) are, amongst other, resistant to fuels and oils[2], but they show substantially inferior thermal properties and potentially produce HF during thermal degradation.[3] Hopefully, blending PDMS and FS would then be a convenient way to combine the pros of each polymer[4].

This work presents our study on the blending and crosslinking of PDMS/FS mixtures. Thermal and mechanical properties of the final elastomers were studied, as well as solvent resistance. Crosslinking using different organic peroxides, showed to be a major parameter for achieving good mechanical properties. All these investigations suggested that the blend containing 30 parts of FS best fulfilled expectations in term of thermal stability, swelling and mechanical properties.

References

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Hydrophobic/hydrophilic incompatibilities make it very difficult to bind silicones to saccharides. Boronic acids are known to form complexes with a wide variety of diols including various types of saccharides [1]. Previously, we demonstrated that boronic acid/diol interaction could be utilized to link silicones to various sugars, as was demonstrated with silicone polymers that incorporate boronic acids as either pendant or end groups [2]. When mixed, these materials polymerized to form elastomers via entirely non-covalent interactions. We have also shown that silicone mono-boronates are able to bind saccharides [3].

We have extended this approach to elastomers that are also covalently linked (using hydrosilylation); with a focus on the ability of silicone boronic acid elastomer surfaces to bind different types of saccharidic materials including monosaccharides, polysaccharides, and glycosylated proteins vs non-glycosylated proteins. Silicone boronic acid elastomer surfaces were exposed to fluorophore tagged saccharide solutions allowing saccharide-boronic acid complexation. The efficiency of binding was established, after washing, with fluorescence microscopy and a quartz crystal microbalance. Contact angle measurements reflected an associated change in surface wettability due to saccharide binding. The affinity of binding, and responses to the surface will be described.

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Addition polymerization of norbornenes bearing trialkoxysilyl groups

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The glassy polymers containing Si-O bonds could be employed for membrane gas separation of hydrocarbon mixtures. For instance, addition poly(3-(tris-(trimethylsiloxy)silyl)tricyclononene) possesses a high butane/methane permselectivity [1]. In this work we successfully synthesized a series of metathesis and addition polynorbornenes bearing trialkoxysilyl groups and studied their properties.

The 2-stage synthesis of new monomers, 3-trialkoxysilyltricyclo[4.2.1.0{2,5}]non-7-enes (alkoxy = OMe, OEt, OPr, OBu), is described. The synthesis was realized by means of [2$sigma$+2$sigma$+2pi]-cycloaddition of quadricyclane and vinyltrichlorosilane followed by treating the product with corresponding alcohol. This monomer series proved to be active in ring opening metathesis polymerization (ROMP) and addition polymerization (AP). For the ROMP 1-st generation Grubbs catalyst was used. The formed polymers turned out to be amorphous, high-molecular weight, and glassy or rubbery products depending on the length of alkoxy group. For AP different Pd-based complexes were used as catalysts with various B-based compounds, as cocatalysts. The optimal conditions of AP were found for this series of monomers. Amorphous high-molecular weight glassy polymers were successfully obtained and studied.

Additionally, the synthesis of a new silatrane-containing monomer, 3-silatranyltricyclo[4.2.1.0{2,5}]non-7-ene, was developed. This monomer was obtained by reaction of 3-trimethoxysilyltricyclo[4.2.1.0(2,5)]non-7-ene with equimolar amount of triethanolamine. The silatrane-containing monomer turned out to be active in ROMP, which resulted in the formation of amorphous high-polymeric glassy polymer. AP in the presence of Pd-complexes with various B- or Al-organic compounds led to the formation of insoluble oligomers and polymers. This work was sponsored by RSF grant No. 17-19-01595.

References
OL18: Dynamic Covalent Silicone Network Polymers: Imine-Based Elastomers

Robert Bui; Michael A. Brook
McMaster University

The majority of silicone elastomers are thermoset polymers that possess useful properties such as resistance to heat and photodegradation. However, thermoset elastomers lack the ability to be remolded or recycled. By contrast silicone polymers that crosslink with reversible bonds involving hydrogen bonding, or metal-ligand interactions can respond to external stimuli such as heat, light, or addition of catalyst to promote new permanent or reversible bond formation. This provides the ability to tune the properties of the elastomer after its formation or to repurpose it.

Herein we report the preparation of silicone polymers that undergo dynamic, covalent imine-based cross-linking through Schiff-based condensation of bis(3-aminopropyl)polydimethylsiloxane and an aromatic aldehyde. The elastomers have mechanical properties comparable to commercial thermoset silicone elastomers and are remarkably tolerant to hydrolysis across a broad pH range (pH 3-12). The dynamic nature of imine bonds in the polymer network was confirmed by observation that the elastomers exhibit self-healing properties. The rate of dynamic exchange is dependent on solvent polarity as determined by mechanical analysis on materials and nuclear magnetic resonance in various solvents; faster imine-bond exchange was observed in polar solvents than non-polar solvents. Further modifications to increase the polarity or the amine content may promote bond exchange and self-healing capabilities. The suppression of imine exchange is achieved by reduction of the imine bonds with the addition of hydride or by boron-catalyzed hydrosilylation.
Dielectric elastomers are a promising category of smart materials, which may find application within many fields such as soft robotics, wave-energy harvesting and loud speakers [1]. A dielectric elastomer consists of a thin, stretchable polymer film sandwiched between two compliant electrodes. When an external voltage is applied to the electrodes, an electrostatic pressure across the elastomer is generated, which will cause the electrodes to attract one another. Thereby the thickness of the elastomer is decreased and the cross sectional area of the elastomer is increased. When the voltage is switched off, the elastomer regenerates its original shape.

Several electrical aging mechanisms are known to occur during operation; some cause fast breakdown while others cause slow degradation of the dielectric elastomer. One of the most significant fast aging mechanisms is thermal breakdown. Thermal breakdown initiates when the heat produced within the elastomer, mainly joule heating, exceeds the heat loss to the surroundings. This may be either locally or macroscopically [2].

We strive to enhance the understanding of thermal breakdown in dielectric elastomer by performing numerical simulation of the actuation of dielectric elastomer transducers in stacked configuration. Multiple simulations using experimental data for PDMS have been performed using COMSOL Multiphysics, from which the key parameters affecting thermal breakdown have been identified. In this presentation we will present the findings and identify the optimal operating conditions for a PDMS dielectric elastomer in order to minimize thermal breakdown.

**References**

OL20: Effect of Filler Content, Particle Size and Size Distribution on the Permeability of Soft Magnetic Liquid Silicone Rubber

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In this work polymer bonded soft magnetic composites (PBSMC) of liquid silicone rubber and different soft magnetic fillers were produced. A characteristic degree of filling was revealed appearing in density, viscosity and magnetic permeability. A simple model is proposed to describe the magnetic permeability as a function for the degree of filling requiring only one adjustable parameter $k$. This parameter takes into account particle properties like magnetization, particle size and size distribution [1]. Originating form this further size fractions of the filler with the strongest impact on permeability were produced by milling and sieving. The actual particle size was determined using a video microscope. At a constant degree of filling a correlation was found between the size of the particles and the adjustable parameter $k$. By mixing small and large fractions suggestions are made for the mathematical form of a governing mean, taking into account the particle size distribution. The obtained mean shows self-consistent behavior and holds for different mixtures. Therefore the simple one-parameter-model can be modified to predict the permeability of PBSMC from the particle size distribution and the degree of filling.

References

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OL21: Glycerol-silicone elastomers as active membranes for wound dressings and beyond

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A recently reported, two-phase glycerol-silicone elastomer is shown to be tunable with respect to the order of release kinetics (zero- or first-order) of actives soluble in the glycerol phase simply by changing glycerol content.[1,2] Importantly, release from the elastomer shows no burst effect. In this approach discrete glycerol domains embedded within a silicone matrix are used as reservoirs for active substances. Upon contact with aqueous media the active substances are released from membranes exhibiting zero-order, near zero-order or first-order release kinetics. Various parameters influencing the drug delivery process like glycerol content, glycerol domain size or membrane thickness are thoroughly investigated elucidating guidelines for creating membranes capable of delivering active substances at desired rates. Additionally, the material was proved to exhibit superior water vapor transmission rates and to absorb significant amounts of liquid water (up to 1850 % of sample mass), features that can be tuned by manipulation of the membrane structure.

References

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Electroactive polymers (EAPs) are a class of smart materials able to convert electrical energy into mechanical energy or vice-versa mechanical energy into electricity. These two application pathways require materials with inherently different properties, e.g. a low Young’s modulus is needed for actuators and large strains are mandatory for energy harvesting. A common parameter should be taken into consideration, the dielectric permittivity of the dielectric elastomer. Commercially available silicone elastomers generally meet the requirements in terms of mechanical characteristics but exhibit low values for dielectric permittivity. Siloxanes are versatile polymers that can be tailored as required to obtain the desired materials for purposed applications. Thus, the main aim falls to improve the dielectric permittivity without inherently diminish properties of interest. As dielectrics for actuator applications, two synthesized poly(dimethyl-co-methylvinyl)siloxanes-alpha,omega-diols, having approximately the same molecular mass but different percentage of vinyl groups, were functionalized via thiol-ene “click” reactions with 3-chloro-1-propanethiol. The resulting polar silicones were cross-linked by condensation reactions obtaining soft elastomers which exhibited giant actuation strains, up to 80% at 45 MV/m. Regarding energy harvesting, polymer composites were purposely designed, by choosing a high molecular, in lab prepared PDMS having low percentages of ceramic nanotubes as fillers, in order to obtain a generator with 8.8% efficiency.
OL23: Silicone surfactants based on natural hydrophiles

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Silicone surfactants are widely used in demanding interfacial applications, including polyurethane foam stabilizers, and agricultural adjuvants. The most common hydrophilic components are polyethers, particularly poly(ethylene glycol) (PEG). This hydrophile has drawn increasing environmental concern. We reasoned that natural hydrophiles could be used to replace polyethers in silicone surfactants. As is common with silicones, the major challenge is overcoming the ‘oil/water interface problem’ during synthesis. We will present a variety of straightforward approaches to the preparation of natural silicone surfactants using azide-alkyne and thiol-ene chemistry click chemistry, lactone-amine reactions, Diels Alder reactions and Michael additions; the use of conventional hydroxyl protection can be avoided in these processes. The hydrophiles chosen include mono, di- or polysaccharides and amino acids. The relative efficiency of these synthetic approaches will be discussed and the surface activities of the compounds will be compared.

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OL24: Insight into the thermal degradation behaviour and products of commercial cross-linked PDMS

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Silicone elastomers are employed in many different fields from biomedicine to electronics due to a plethora of unique features. In particular, the thermal stability is fundamental with respect to the reliability and the performance of silicone-based devices. This remarkable resistance upon high temperatures is due to the inherent strength of the siloxane bond, the considerable flexibility of the backbone, and the entropically higher stability of the cyclic degradation products compared to the linear original chain [1]. Keeping in mind the vast majority of work done so far on the degradation of silicones [2,3], the goal of this study is to achieve a deeper insight into the thermal degradation mechanism of commercial silicone elastomers with the main aim of translating it into the complex, coupled thermal and electrical breakdown processes that dielectric elastomers undergo. A systematic analysis of the thermal behaviour was carried out using thermogravimetric analysis (TGA) on the pure poly(dimethyl siloxane) network with different crosslinking ratios performed in either inert atmosphere (pure thermal degradation) or air (thermo-oxidative degradation). Extraction of the samples in heptane was exploited in order to remove the non-bonded PDMS chains and determine to which extent the thermal degradation is influenced compared to the pristine elastomers. The core of the work was the accurate recovery and characterization of the volatile and non-volatile degradation products of the thermally treated elastomers, aiming at the elucidation of the mechanism and the extent of degradation through the combination of different techniques such as size exclusion chromatography and infrared spectroscopy.

References

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P1: Electrical breakdown phenomena of dielectric elastomers

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Silicone elastomers have been heavily investigated as candidates for dielectric elastomers and are as such almost ideal candidates with their inherent softness and compliance but they suffer from low dielectric permittivity [1]. This shortcoming has been sought optimized by many means during recent years. However, optimization with respect to the dielectric permittivity solely may lead to other problematic phenomena such as premature electrical breakdown. In this work, we focus on the chloro propyl functionalized silicone elastomers prepared in Madsen et al [2] and we investigate the electrical breakdown patterns of two similar chloro propyl functionalized silicone elastomers which break down electrically in a rather different way as well as we compare them to a silicone based reference. Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) are used to evaluate the elastomers before and after electrical breakdown. It was shown the chemically very similar silicone elastomers broke down electrically in very different ways. These observations emphasize that the modification of the silicone backbone may open up for completely new possibilities for stabilizing the silicone elastomer electrically. In order to tailor the elastomers, more knowledge is needed but these copolymers pave the first path towards a better understanding of the complex connection between electrical and thermal stability. Minor changes in the polymer backbone structure result in changes in electrical breakdown patterns and understanding why is crucial for enabling design for extraordinarily stable elastomers and thus ultimately reliable dielectric elastomer based products.

References

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P2: Functionalization of SSBR by [bis(trihydrocarbylsilyl)amino]-substituted styrene derivatives

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4: Synthos S.A., St. Chemików 1, 32-600 Oświęcim, Poland

Rubber designed for the manufacture of tire treads has to be characterized by suitable properties, the most important of which are good wet grip performance, high wear resistance and rolling resistance [1]. In order to achieve the best parameters, compositions created on the basis of styrene-butadiene rubber together with butadiene rubber and fillers such as carbon black and silica commonly are applied. However, the improvement in rubber functional properties is not possible without achieving a proper dispersion of the aforementioned fillers in the elastomer matrix. Therefore, to meet this goal, incorporation of appropriate functional groups into the polyene chain, able to interact physically or form covalent bonds with groups present on surfaces of carbon black and silica is required [2].

In this communication, the application of novel bis(trihydrocarbylsilyl)amino-functionalized styrene derivatives as co-monomers for functionalization of synthetic rubber is presented. The above-mentioned compounds bearing in their structure (Me3Si)2N-SiMe2-CH2-CH2-Si-(CH2)- moiety seem to be very promising. Despite the fact that they generally are hydrolytically stable, under appropriate conditions they are able to hydrolyze partially with the formation of reactive silanol groups (HOSiMe2-(CH2)-, which in a further step are able to interact covalently with silica via [(SiO2)O3Si]-O-SiMe2-CH2- bonds formation. The remaining (Me3Si)2N-SiMe2-CH2-CH2- functionalities can increase the dispersion of carbon black due to non-covalent interactions. The styrene derivatives equipped with such functional groups of unique properties have been employed in anionic polymerization of styrene and butadiene in solution and the influence of such functionalization on physico-mechanical properties of macromolecular products additionally will be discussed [3].

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P3: Heterogeneous bimodal condensation elastomers: an opportunity for many applications

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Recently many application areas, such as automotive, electric and electronics, gaskets, domestic appliances, fabric coatings, baby bottle nipples and medical devices, highlight the employment of silicone elastomers. Indeed, they are increasingly being used to substitute for organic rubbers due to the notoriety of their unique properties, namely high and low temperature stability, inertness (no smell or taste), low toxicity, colorability and transparency, combined with good electrical properties. [1] With this in mind, the importance of the development of functional polymers comes out on top in order to expand the application range of a given polymer. [2]

PDMS elastomers are known for their high extensibility, high thermal stability, low surface tension and chemical and biochemical inertness. When two polymers with significantly different molecular weights are mixed together, the resulting network, so-called bimodal network, exhibits superior mechanical properties compared to traditional elastomers reinforced with fillers, namely high tear resistance, extensibility, ultimate strength and retard of rupture process. [3]

In this work, bimodal condensation silicone elastomers (where condensation refers to the curing reaction) were created as heavily cross-linked short PDMS chains joining long PDMS chains (testing different mass ratios) in two-step procedure, in order to manufacture thin heterogeneous bimodal networks characterized by regions with high cross-linking density. The resulting elastomers were investigated with respect to rheology, tensile and tear strengths, as well as the curing conditions were optimized, taking into account the dependency of mechanical properties on the atmospheric humidity level.

References

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P4: Self-healing dielectric silicone elastomers with high dielectric permittivity and good mechanical properties

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Silicone elastomers find their use in many applications like actuators or generators. Nowadays, the desired properties for an effective utilization of these materials in energy transducers is, amongst others, high permittivity, low Young’s modulus and good mechanical properties, as well as ability to self-heal after electrical breakdown or any kind of damage.[1] One way to implement self-healing properties in such material is creation of interpenetrating ionic network in silicone network. This approach has an advantage in a simultaneously increase of relative permittivity. As the ionic network amino- and carboxylic acid- functional silicone can be used, where the proton exchange between amino and acids groups enable cross-linking and also healing after damage.[2]

In this work, ionic networks with different molecular weight and concentration of -COOH and -NH2 functional groups were mixed either with commercial condensation silicone or with mixture of hydroxy-terminated PDMS and methyltrimethoxysilane crosslinker. In previous work by Madsen F. B. et al.[3], it was found that samples with ionic network consisting of low molecular weight amino- functionalized silicone (AMS-162, f=4) are rather stiff. Therefore ionic networks consisting of high functional and high molecular weight amino- functionalized silicone (AMS-1203, f=14) were investigated as candidates for interpenetrating polymer networks with good self-healing ability and sufficient permittivity, without the negative effect on the samples stiffness. The samples were tested by means of rheology, dielectric spectroscopy, thermal gravimetric analysis, infrared spectroscopy and scanning electron microscopy and finally the optimal composition was evaluated.

References
P5: Microstructure versus mechanical properties of original silicone/thermoplastic elastomer blends

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Silicones are important materials in the transportation industry for their many exceptional properties such as stiffness, damping, or linear mechanical behaviour in a broad range of temperatures. In order to improve these key material properties, specific additives such as silicone-urethane copolymers or silicone-urea copolymers [1] are believed to be of interest.

Here, different blends of a silicone gum and different silicone thermoplastic elastomers (TPEs) are presented. Processing, characterization and mechanical testing were done with several kinds of silicone-urea copolymers: two commercial TPEs (which have interesting damping properties [2,3]) and an original TPE structure, that was home-synthesized. The relationships between the microstructure, morphology and the mechanical properties are presented here with the help of imaging (TEM) and mechanical testing (tensile tests and temperature and strain sweeps in DMA).

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P6: PDMS containing carboxyl groups

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PDMS has a unique set of properties, such as thermo stability, UV and ozone resistance, biological inertness and etc. However, due to the weak intermolecular interaction, modification of siloxane rubbers and improving their physical and mechanical properties is an urgent task. To solve this problem, it can use the introduction of polar substituents, forming hydrogen bonds, in the siloxane chain. To create materials with improved characteristics, we propose to use PDMS modified with carboxylic acid residues having different types of protecting groups, which can be removed under different conditions. We suggest that presence of these groups in the PDMS chain will allow to increase the MW of polymer at the first stage of curing and to get a three-dimensional network at the second stage. A number of PDMS copolymers containing from 0,1 to 15 % mol. modified siloxane units and molecular weight from 1600 to 20000 was synthesized. Thermal and rheological properties was investigated.
P7: Electrochemical determination of endocrine disrupting chemical by using electrode modified with imprinted sol-gel particles

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With the development of industry, various industrial waste chemicals are being emitted into environments and some of them are found to be environmental endocrine disrupters and carcinogens. Therefore, an efficient determination method is required for monitoring the levels of these chemicals. Among various analytical techniques, electrochemical sensor should be a promising technique with the advantage of reliability, fast response, cheap instrument, low cost, simple operation, timesaving, high sensitivity, good selectivity and real-time detection in situ condition. A new trend in analytical chemistry is to develop novel sensors based on molecularly imprinted polymers (MIPs). Since the development of sol-gel technology, there has been increasing interest in use of imprinted polymers as thin films for electrochemical sensor devices. Generally, silica gel is prepared by mixing functional precursor, sol-gel matrix forming monomer and the template ion or molecule [1, 2].

In the present work, a modified carbon paste sensor electrode was constructed for the selective electrochemical detection of an endocrine disrupting chemical (EDC) by using molecularly imprinted polymer and a sol-gel network. The sensitivity of the electrode was improved by using multi-walled carbon nanotubes (MWCNTs) during the preparation of carbon paste due to their unique properties such as large surface area, strong conductivity, adsorptive and catalytic ability. The electrode prepared by the combination of MWCNTs with imprinted sol-gel offered an attractive way to enhance the sensitivity and stability of the electrochemical sensor. The proposed electrode was used for determination of EDC in real samples successfully.

References
P8: A new class of catalysts for hydrosilylation reaction

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Based on silicon and oxygen backbone, silicones are high-performance polymers. Their properties can be tuned by modifying organic groups on silicon atom. To build the polysiloxane chain, the hydrosilylation reaction, i.e. addition of hydrosilane or hydrosiloxane moiety across a carbon-carbon double bond, is a key reaction not only for synthesis of functional silanes of polysiloxanes but also for the manufacturing of silicone materials. Although hydrosilylation has been known for more than 50 years, industrial catalytic systems are mainly based on Platinum (chloroplatinic acid, Karstedt catalyst). [1]

Up to date, focusing on activity and selectivity, Karstedt catalyst remains the best catalyst known for hydrosilylation in silicon media. For many reasons, in particular economical ones, the development of original platinum-free catalysts for the hydrosilylation reaction and crosslinking of silicone materials is nowadays an important target. Alternatives catalysts based on other metals such as rhodium, iridium, ruthenium, nickel and more recently iron or cobalt have been also developed. [1],[2]

In the present work we investigated metal complexes bearing chelating acetylacetonate ligand based on first row late transition metals for hydrosilylation of olefins (such as octene...) and crosslinking under non-inert atmosphere silicone materials.[3]

References

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P9: Evaluation of the electromechanical transduction performance of silicone elastomers filled with bariumtitanates of different particle sizes

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Mimicking the complex motion sequences of human muscles is a great challenge in science. A promising approach to surrogate a muscle comprises the application of electroactive polymers. By applying an electric field to an electroactive polymer, it is possible to change the shape of the polymer and therefore the imitation of difficult movements can be realized. Especially, the field of research on dielectric elastomers (DE) is growing rapidly due to the large strains that can be achieved and the good overall performance. DE can convert electrical to mechanical energy (actuation mode) and vice versa (generator mode). Based on the fact that a rubber-like behavior of the polymer is desired in many applications, liquid silicone rubbers (LSR) play an important role in the field of DE [1].

It is known in the literature that the actuation is limited by the dielectric permittivity of the DE. In respect of the rather low dielectric constant of LSR a possible way to increase the permittivity and hence the dielectric properties is given by the addition of ceramic fillers with a high dielectric constant, e.g. barium titanate [2].

This work evaluates the electromechanical properties of two different silicone elastomers (room and high temperature vulcanizates) filled with bariumtitanates of different particle sizes. Thus, it is possible to model the permittivity as well as the transduction performance in dependence of the filling degree and the particle size of bariumtitanate for the first time.

References

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P10: Evaluation of the diffusion properties of silicone elastomers related to the crosslinking density and of the mechanical weakening due to silicone oil up-take

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The continuing discussion on safety and quality of silicone breast implants with respect to the increased amount of potentially toxic low molar mass components in the PIP silicone breast implant gels is one of the driving factors why this study turned into focus [1, 2, 3].

The diffusion coefficients of silicone oils into silicone elastomers were analysed by means of the crosslinking density and the penetrant size. The study was focused on the diffusion of cyclic siloxanes, octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5) and Dodecamethyl-cyclohexasiloxane (D6) due to their potential occurrence in silicone breast implants [2]. The analysis of the diffusion behavior was carried out with tailor-made silicone elastomer samples varying in crosslink density. Therefore, sorption experiments according to past studies of Gedde and his team were performed [4]. The subsequent evaluation of the sorption data yields the corresponding diffusion properties. Based on the diffusion coefficient related to the crosslink density a model was developed to describe the diffusion behavior.

In addition, the mechanical properties were analysed of samples with various degrees of swelling. Therefore tensile tests were performed with dog-bone shaped silicone-elastomer samples after certain swelling times from 5 minutes up to 72 h. Besides of the three already mentioned cyclic siloxanes, linear siloxane oils of different molar mass were used for the swelling. In conclusion the results of the mechanical behaviour of the silicone elastomer were evaluated in relation to the sorption properties.

References


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Dielectric elastomers (DE) are utilized as soft electroactive polymers (EAP) for actuators, sensors or generator applications to transduce mechanical to electrical energy. They are characterized by the ability of changing shape while an electrical field is applied. Indeed, this effect is largest for electrical fields near the electrical breakdown strength, which requires a further investigation of the influences and mechanisms of electrical breakdown in DEs as limiting factor of application.

This paper investigates the influences of electrode shape, sample thickness, barium titanate (BaTiO3) as additive and the deformation of the specimen on the dielectric breakthrough strength of the silicon elastomer ELASTOSIL P7670.

We describe a test setup for the measurement of the electrical breakdown strength, which allows testing a multitude of specimen to little effort. The samples have been stimulated via one planar and a hemispherical counter electrode with a variation of three different curvature radii. To identify the influence of the sample thickness, specimen with a thickness ranging from 0.2 mm to 0.7 mm have been tested. The data clearly shows the compression of the silicon elastomer as the dominant factor with regard to dielectric strength. An increase of almost one magnitude from 50 V/μm up to 431 V/μm has been observed. Finally we present a statistical regression model, which displays the obtained data and allows us to estimate the anticipated dielectric strength for a given deformation.
Unlike living organisms, synthetic materials are not able to recover from damages and possess therefore a limited lifetime [1]. To counteract this fragility, supramolecular polymers have shown a great interest since a couple of decades thanks to their reversibility and thus their reusability. Recent studies also focused on the emergence of new materials that self-heal without any external stimulus; to this aim supramolecular materials are of particular interest [2].

Starting from published systems [3,4], we first set up a fundamental study by reacting amino-PDMS with urea, a system that may lead to various functional groups likely to interact through H-bonding. Silicone-based systems were considered here for their hydrophobicity, flexibility and thermal stability. The influence of the nature of the associating groups on the physicochemical properties is investigated in this study. Other parameters such as chain length and hydrophilic to hydrophobic ratio are also included in this reasoning. Different analytical studies were carried out in order to determine the chemistry (NMR, IR and SEC) and assess the physicochemical properties (rheology, TGA, DSC).

With a complete understanding of supramolecular interactions, prospects of the study are to endow polydimethylsiloxanes with autonomous self-healing abilities.

References
P13: Synthesis and characterization of poly(methylhydrosiloxane) and its copolymers

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Poly(methylhydrosiloxane) (PMHS) is an attractive organosilicon polymer since its repeat unit contains reactive Si-H groups. Therefore PMHS can be relatively easily functionalized and thus converted to the compounds tailored for selected applications.

PMHS is available commercially, but its average molar mass does not exceed 3200 g/mol which may be a drawback. The aim of this research was to develop a simple and reproducible method to synthesize macromolecular polymer with controlled, predetermined average molar mass.

First, PMHS was prepared by cationic ring-opening polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D4H) in emulsion as proposed by Ganachaud and co-workers [1]. Dodecyldiphosphonic acid was used as surfactant and initiator of the process. Then the method was modified by using various amounts of hexamethyldisiloxane which served as the polymer chain length regulator.

The average molar mass of the obtained samples was examined by size exclusion chromatography with toluene as an eluent. 29Si NMR analyses confirmed the formation of linear chains and their termination by \((\text{CH}_3)\text{Si}\) moiety. FT-IR spectra contained all the bands characteristic for PMHS. Gas chromatograms of the mixture separated under vacuum confirmed the presence of unreacted D4H and volatile cyclic compounds in the crude polymerization product.

Finally, it was attempted to use the developed method to synthesize block copolymers containing methylhydrosiloxane and dimethylsiloxane units. The synthesis of PMHS of controlled average molar mass and its copolymers can be very useful to modify and functionalize linear polysiloxane chains in future.

The work was financially supported by Polish National Science Center (NCN) project number 014/13/B/ST5/01924

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P14: Polysiloxane and polysiloxane-silazane networks with incorporated palladium particles

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Polymer matrices with introduced metal particles have been intensively studied for more than two decades. Systems that can be applied as heterogeneous catalysts draw particular interest. In most studies, however, organic polymers have been used as supports for metallic catalysts even though polysiloxanes, especially the cross-linked ones, are perfectly suited for such purpose.

The work presents our investigations on incorporation of palladium particles into the networks obtained by cross-linking of poly(methylhydrosiloxane) with 1,1,3,3-tetramethyl-1,3-divinyldisiloxane or 1,1,3,3-tetramethyl-1,3-divinyldisilazane. The reactions were carried out at molar ratio of Si-H : Si-vinyl groups equal to 6 : 1. Owing to this, unreacted Si-H groups remained in the cross-linked systems as was confirmed by FTIR spectra. FTIR spectroscopy also showed that Si-H groups served as reducing agents upon incorporation of palladium into the networks, performed using palladium(II) acetate solution in THF.

The presence of metallic palladium in the systems was established by X-ray diffraction and X-ray photoelectron spectroscopy. Sizes and distribution of Pd particles on the surfaces of the samples was examined by SEM. Additionally, selected samples were pyrolyzed in inert atmosphere (Ar or N2) at 600°C and 1000°C. In this way, SiCO or SiCNO materials containing Pd particles were obtained. Catalytic properties of the samples before and after pyrolysis were studied using isopropyl alcohol conversion as test reaction.

It was found that nitrogen atoms present in polysiloxane networks facilitate incorporation of Pd particles and are advantageous for catalytic activity.

The work was financially supported by Polish National Science Center (NCN) project number 014/13/B/ST5/01924

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P15: Synthetic Routes to Silicone-Modified Soybean Oil Copolymers

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Continued concern over the impact of petrochemicals on the environment has led to a push to create materials using the principles of sustainability, while not compromising physiochemical properties of the products. Soybean oil is a high volume, commercial unsaturated triglyceride predominantly used for cooking applications although it has a long history in polymeric materials such as linoleum. We were curious to explore the possibility of increasing the value and utility of this green starting material by modifying it with silicone polymers.

The double bonds present in soybean oil serve as the perfect platform for introducing synthetically useful siloxane functionality via thiol-ene click reactions, or through a peroxide catalyzed ene reaction. (3-Mercaptopropyl)trimethoxysilane and trimethoxyvinylsilane were grafted onto soybean oil use thermal thiol-ene, and peroxide-initiated ene reactions, respectively. The resulting alkoxysilane could then be used in two different reactions: The Piers-Rubinsztajn reaction (PR) and Room Temperature Vulcanization (RTV, moisture cure). The B(C6F5)3-catalyzed PR reaction, using the modified soybean oil and hydride-containing polydimethylsiloxane (PDMS) led to foams, while RTV cure with silanol containing PDMS in the presence of tin gave elastomers. In both cases, it was possible to tune the properties of the products simply by controlling the length of crosslinker. A comparison between this process and the direct thiol-ene reaction of soybean oil with mercaptopropylsilicones will be made.

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The insertion of implantable devices such as catheters requires lubricious surfaces. Silicone elastomers have many beneficial properties and are widely used in biomedical applications (e.g., Foley catheters, pacemaker leads, breast implants); lubricity is not one of them. Pullulan, a polysaccharide formed naturally by many microorganisms such as Aureobasidium pullulans, forms a very lubricious mixture with water. We reasoned that, if pullulan could be slowly released from silicone elastomers, the lubricity could be enhanced.

Pullulan was dispersed in uncured silicone rubber using glycerol as a carrier. The materials were cured using condensation cure or hydrosilylation. The coefficient of friction of the resulting elastomers was dramatically reduced once immersed in water due to the slow release of pullulan.

Implant failure due to bacterial infection is of notable concern in the biomedical industry. We were initially assured that pullulan would not be problematic in this regard, because it has been shown that bacteria are not able to process it. Unfortunately, the glycerol carrier was found to support the model bacterium Escherichia coli. Attempts to overcome biofilm formation by the co-release of antibacterial agents will be described.
P17: Application of silicone based elastomers for manufacturing of Green Fiber Bottle

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Due to ever-increasing demand of sustainable products, eco-friendly packaging solutions are finding their importance in the paper packaging industry [1]. Green Fiber Bottle (GFB) is an alternative to plastic, glass and metal based packaging for beverages. The manufacturing of paper bottle is a two-stage process, where the wood fibers are first thermoformed in the desired shape followed by drying of the formed geometry [2]. To ensure the robustness of the bottle and to avoid shrinkage of cellulose fibers, the wet-formed bottle is pressurized using a silicone core. The core is inserted inside the drying tool and inflated. This keeps the wet bottle under pressure thereby enhancing formation of good hydrogen bonds, and hence providing good strength. The feasibility of the tool design concept is supported with Finite Element Model. The hyperelastic behaviour of silicone is defined by the deformation energy function (W). To simulate the inflation action of the core, Yeoh’s model is used for modelling of W. The strength of the GFB is correlated with the pressure the bottle can hold and the cut off burst pressure from experiments is also reported in this work.

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P18: Mechanical properties of silicone breast implants under compression load and its effect on the implant shape and the shell material

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In this study the mechanical behavior of gel-filled silicone breast implants were examined as well as the mechanical properties of the implant shell itself. At first the implants were tested under compression load in two different ways, with cyclic load to assess the implant shape retention and unique with maximum load until rupture. Subsequently the implant shell material was analyzed by tensile test on dumbbell-shaped specimens. The results are presented by colored contour plots which allow a detailed view on the measured values of the samples.

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Ideal polydimethylsiloxane (PDMS) elastomers for dielectric elastomer uses are characterized by inherent softness and good tensile strength [1]. Such elastomers can find application as electroactive polymers for manufacture of artificial muscles. Preparation of soft PDMS network is not straightforward because polymer chain entanglements act as cross-linking points contributing to an increase in the elastic modulus. The PDMS bottlebrush architecture increases the diameter of the polymer chains as well as decreases the number of entanglements and thus introduces softness beyond what is capable with traditional silicones [2]. Hence, bottlebrush PDMS elastomers were synthesised and tested in terms of application as electroactive polymers. Cross-linking of long bottlebrush PDMS backbone with high-molecular weight cross-linking agent allowed for preparation of soft elastomers. Soft PDMS elastomers characterized by good tensile strength and low storage modulus were successfully prepared via simple one-pot synthesis without utilization of any solvents. Detailed characterization revealed that bottlebrush PDMS elastomers are promising candidates as electroactive polymers.

References
P20: Magnetically Activated Microcapsules - Preparation and Characterization

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Microencapsulation gives an advantage of releasing enclosed material on demand. A PDMS cross-linker has been encapsulated within a polymer shell with aim of controlling formation of a PDMS network. The utilization of magnetic nanoparticles (MNPs) in hyperthermia for cancer treatment, based on heat dissipation mechanism of MNPs in an alternating magnetic field (AMF) [1], has inspired us to design magnetically activated microcapsules.

Several types of MNPs have been encapsulated together with the cross-linker via phase separation technique [2]. Mass content of the MNPs, morphology and reactivity of the microcapsules were investigated. The magnetic microcapsules were also subjected to the alternating magnetic fields at a wide range of frequencies with the aim of releasing the enclosed cross-linker. The microcapsules containing the MNPs were successfully prepared without compromising the impermeable nature of the microcapsules. The nanoparticles were mainly located in the core of the capsule and the shell’s structure remained intact. Exposure of the microcapsules to the AMF at various frequencies allowed for determination of activation conditions.

References

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P21: Efficient transition-metal catalysts for hydrosilylation using a strong donating silylene ligand

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Introduction of new ligands can often drastically modulate the reactivity of metal-centers. Particularly, N-heterocyclic carbene (NHC) ligands are well recognized to be excellent ligands which efficiently stabilize and activate metal centers in different catalytic steps of organic synthesis, such as C-H activation, C-C, C-H, C-O and C-N bond formation[1]. The hydrosilylation reaction has been and remains one of the major challenge from both applied and fundamental points of view, and the well-known Karstedt catalyst 1 is established as a reference in the field[2]. But the NHC-Pt(0) complex 2 shows an enhanced stability and selectivity in the reaction, clearly demonstrating the important role of the ligand.[3]

Our group has recently synthesized a stable silylene 3[4], that proved to be an excellent ligand with a more electron-donating character than that of NHCs. Indeed, a new air stable Pt(0) complex 4 with this silylene ligand presents a remarkable catalytic activity in the hydrosilylation reaction of olefins, rivaling, and even outpacing the Karstedt's catalyst performances. In addition, the new copper complex 5 is active as a catalyst for the hydrosilylation reaction of ketones and exhibits a particularly high reactivity in the case of bulky substrates[5].

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P22: Modeling of energy losses in dielectric elastomers

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Dielectric elastomers are an interesting class of materials that have shown potential for advanced electromechanical applications such as actuators, sensors and generators. The dielectric elastomer consists of an elastomer film sandwiched between two compliant electrodes. When an external voltage is applied the dielectric elastomer is compressed as a result of the generated Maxwell pressure, and when the voltage is switched off the dielectric elastomer will regain its original shape [1]. In order to maximize the actuation strain of the dielectric elastomer high electric fields are required. In addition the thickness of the dielectric elastomer is increased by stacking multiple film layers to increase the mechanical energy storage capacity. Both the increase in layers and the high electric fields results in increased joule heating. Thermal breakdown occurs when joule heating within the system cannot be balanced by the heat dissipated from the surface. The heat generated by joule heating is dependent on several parameters, e.g. the electrical conductivity which is proportional to the heat generation. The electrical conductivity is temperature dependent and increasing the temperature may therefore lead to thermal runaway through a positive feedback loop. In order to determine the trends of how the different parameters affect the occurrence of thermal breakdown a model have been constructed. The model predicts the temperature on the basis of the electrical and thermal conductivity, surrounding temperature, electric field and the number of film layers, and thereby gives an indication of whether a certain design is feasible.

References

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