

Screening of grafting methods for modification of polymer surfaces

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In many cases, it is desirable to have specific surface properties compared to that of the bulk material and this has been a continuous challenge for applications of polymers in particularly biological environments. Development of such surfaces often requires tedious testing of thousands of formulations and therefore such investigations are often conducted with the use of screening platforms. Existing platforms are mainly based on automated systems able to place hundreds of small picoliter scale reactions on a single glass slide under inert atmosphere^{1,2}. The synthetic approach, however, is not necessarily ideal in an industrial setting. Inert atmosphere is complicated to achieve and the small scale do not allow for the investigation of solvents. Additionally, having glass, as a base substrate is a poor representation of the final application for use on grafting of polymer surfaces. To achieve a more industrially relevant process of screening surface modifications, the platform shown in Figure 1 was developed. The system is comprised of three parts: (a) a top plate, (b) the polymer substrate and (c) a stainless steel support. The advantage of this system is that it can endure high temperature and is chemically resistant since the top and bottom plate (a and c respectively) are made of metal and the well size permits addition of solvent. Additionally, the modular structure makes it easy to investigate a range of substrates. The surface modification is conducted directly on the polymer surface via UV-initiated free radical polymerization under ambient atmosphere (see Figure 1, right). Analysis of the surface is enabled by the detachable top plate and allows for investigation using e.g. water contact angle (WCA), x-ray photoelectron scattering (XPS), UV-vis spectroscopy etc.

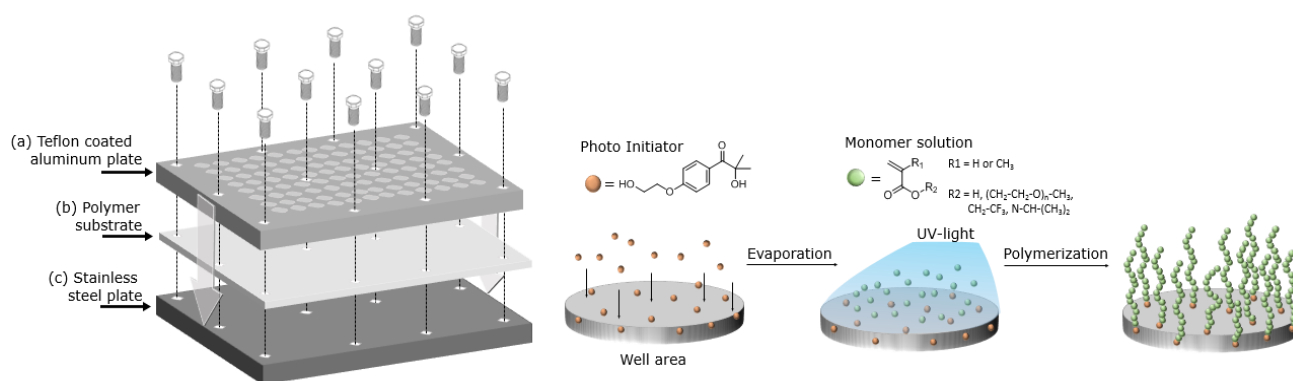


Figure 1: Screening platform consisting of a Teflon coated aluminum plate (a), polymer substrate (b) and a stainless steel support (c) (left). Schematic representation of grafting procedure (right).

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Advanced wound care adhesives with improved moisture handling capabilities

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Broadly, for wounds to heal, a moist, clean and warm environment is required. A moist wound bed easily promotes growth factors and many cell types including epithelial cells to migrate, facilitating wound edge contraction. Thus, appropriate dressings play a significant role to create and maintain such environment.^[1] Silicone adhesives are silicone elastomers which are not fully crosslinked but remain close to the gelation threshold (i.e. with a low crosslinking degree).^[2, 3] Within the field of advanced wound care, silicone adhesives are currently the preferred, state-of-the-art adhesive system due to its gentle skin adhesion properties. However, due to their hydrophobic nature, current silicone adhesives for wound care face challenges when it comes to moisture handling. Here, we propose a novel, skin-friendly, industrially relevant glycerol-silicone hybrid adhesive with improved moisture handling due to the incorporation of emulsified glycerol (Figure 1). Various parameters will be taken into account in order to develop a relevant adhesive, in particular glycerol content, glycerol domain size and adhesive thickness to allow for a controlled moisture absorption.

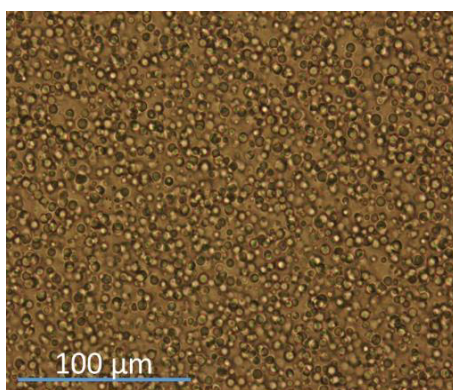


Figure 1: Glycerol domains in the silicone matrix characterized by optical microscope.

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Epoxy Paints – From Molecules to Materials

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A common observed failure of anticorrosive paints used in harsh environments is flaking, which is observed as flakes of paint delaminating from its substrate, as seen on Figure 1. Paint failure by flaking is caused by a struggle between three properties of the paint: adhesion, cohesion and internal stress. Adhesion is the force by which the paint sticks to the surface, and cohesion is the force needed to break the paint apart. Internal stress in a paint arises from changes in dimension, which can be induced by environmental factors such as thermal expansion or contraction. Additionally, a significant amount of internal stress can build up in the molecular network of the paint due to shrinkage caused by molecules reacting and solvents evaporating. When the internal stress built up in the paint becomes larger than the paint's cohesive force, the paint will crack, exposing the substrate to corrosion. Poor control of the curing process can thus lead to poor performance of the paint.

In this project we use Dynamic Mechanical Analysis (DMA) in a dual cantilever setup, as seen on Figure 2, to continuously measure the mechanical properties of paints – e.g. viscoelasticity as a function of time – in order to reveal changes in the material when the small liquid molecules transform into a tough material network. DMA thus allows us to investigate how introducing different functional molecules effect the formation of a cross-linked network and thereby

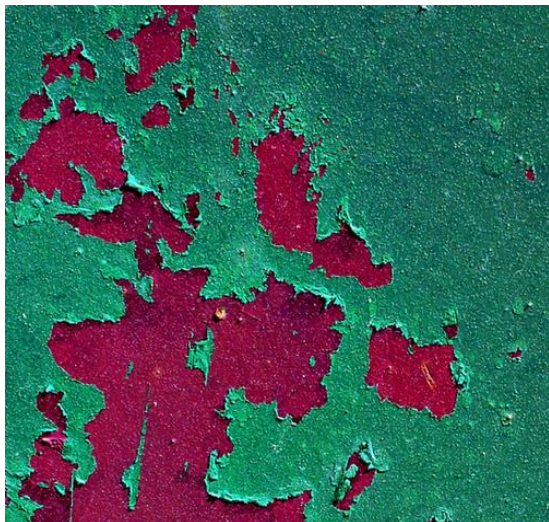


Figure 1: Green paint flaking off a purple substrate

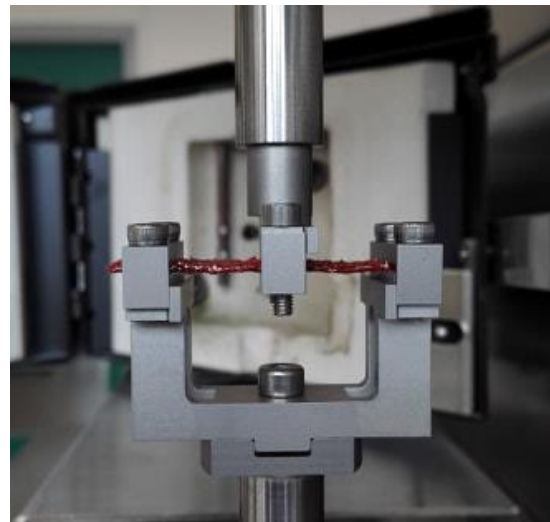


Figure 2: DMA dual cantilever setup with uncured red paint held by a matrix

provides a way to measure and control the curing.

Simulating thermal breakdown in multi-layered dielectric elastomers

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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. 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.

In this work a better understanding of thermal breakdown in a cylindrical stack of multiple dielectric elastomers is obtained by performing simulations in COMSOL Multiphysics®. Several physics modules are used to model the combined effects of joule heating, electromechanical deformation and natural convection. Several hyperelastic material models of PDMS elastomer are compared and various important parameters are studied, to see the influence on point of thermal breakdown for the multi-layered dielectric elastomer stack.

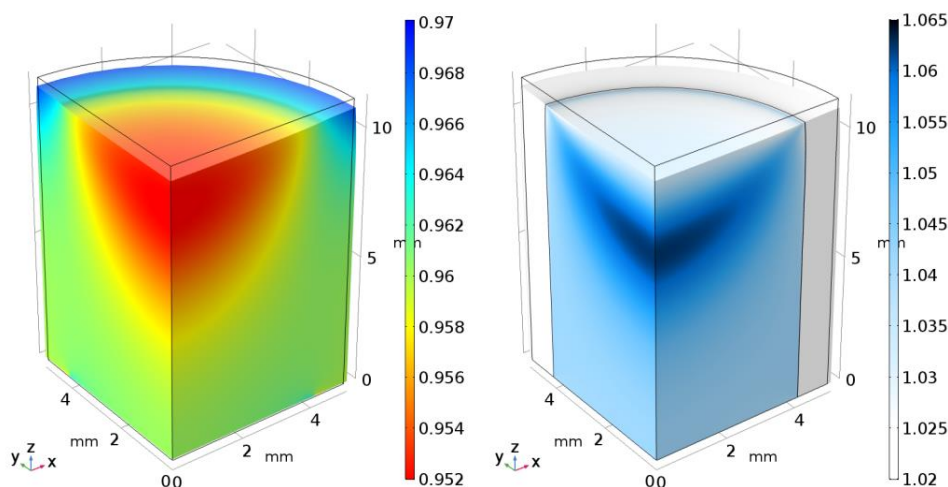


Figure 1: Simulation results from a simulation of a stack of 450 dielectric elastomers. The electrodes are applied in the middle of the stack covering 64% of the total area. The picture to the left displays the stretch ratio in the z-direction, and the ratio of the normalized electric field to the initial electric field is displayed on the picture to the right.

Designing reliable silicone elastomers for high temperature applications

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Silicone elastomers find application in fields ranging, for instance, from soft robotics and electronic skin, to the automotive and the aerospace industries. In addition, the high dissociation energy and the low energy barrier to rotation of the siloxane bond make silicone elastomers suitable for high temperature applications.^{1,2} Reliability and durability are strict requirements for silicone elastomers employed in high temperature applications, and significant effort has been invested by the industrial and the scientific communities into improving their thermal stability. A traditional method to enhance thermal stability is to add heat-resistant fillers in the formulation, but this can lead to loss of transparency and poor filler compatibility with the matrix. Another common way is to chemically modify the silicone network, but this renders the product expensive and, therefore, not appealing at an industrial level. Thus, developing cheap and easy solutions to improve thermal stability of silicone elastomers is a major challenge. This study focuses on determining the role of network structure on the thermal degradation of silicone elastomers.³ Elastomers with different stoichiometric ratios were synthesised to vary the relative fractions of elastic, dangling, and sol structures. Thermogravimetric analysis was used to investigate the thermal degradation behaviour of the silicone elastomers synthesised with different cross-linking densities and to analyse their thermal degradation products. Here, we demonstrate how to optimize the stoichiometric ratio used to prepare silicone elastomers in order to enhance their thermal stability by simple means.

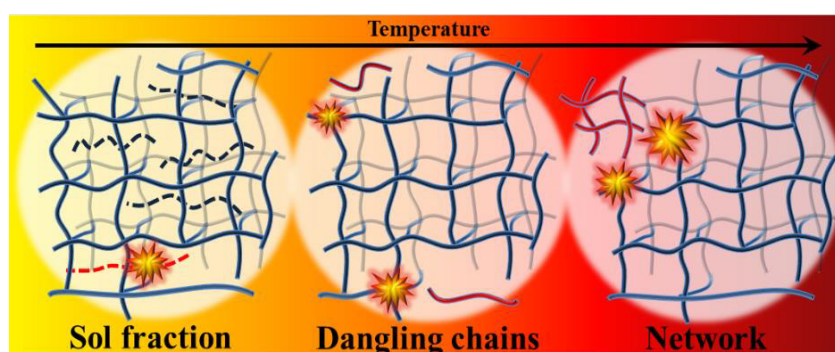


Figure 1: Scheme illustrating how silicone elastomers degrade thermally following a hierarchical trend, depending on the degree of PDMS chain mobility. Thermal degradation involves first unreacted PDMS chains (sol fraction), second pendant structures (dangling chains), and, eventually, the elastically active network chains.

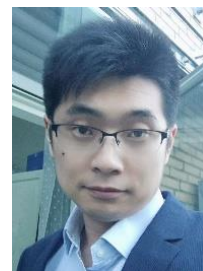
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Hard-soft Thiol-ene Materials without Interfacial Weakness

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During the last century, thiol-ene materials have received significant attention because of the highly efficient reactions of thiols with reactive $C=C$ bonds in allyl or acrylate systems. Thiol-ene materials are a series of materials that can be crosslinked using a suitable photo-initiator and a UV light source. An advantage of thiol-ene materials is that they can be tailored to have specific mechanical properties by controlling the stoichiometry of the mixtures. A layer-by-layer (LBL) structure alternating hard and soft thiol-ene material with a sharp solid interface was prepared by step-by-step. Tetrakis (3-mercaptopropionate) (PETMP) with 1, 3, 5-triallyl-1, 3, 5-triazine-2, 4, 6(1H, 3H, 5H)-trione (TATATO) as the hard segment exhibited strong tensile and compressive strength but had low elongation and weak bending stiffness. A mixture of PETMP and trimethylolpropane diallyl ether (TMPDE) was selected as the soft segment. The interface plays an essential role for the overall mechanical performance of such systems. In particular, the mechanical properties of the interface are crucial to the usability. We designed a chemical method of step-by-step pre-crosslinking to prepare new hard-soft alternate thiol-ene material, which had a similar structure as LBL polymer systems, but results in a significantly stronger interphase (**Figure 1**).

The rheological measurements were carried out using a filament stretching rheometer (*Rheo Filament ApS*). Meanwhile, a high-speed camera was used to capture the fracture process; and the captured optical images were used to measure the local strain of the deformed sample accurately during the crack propagation.

Through the filament stretching study, it is evident that the interface of the alternate materials was strong enough to prevent premature fracture during stretching.

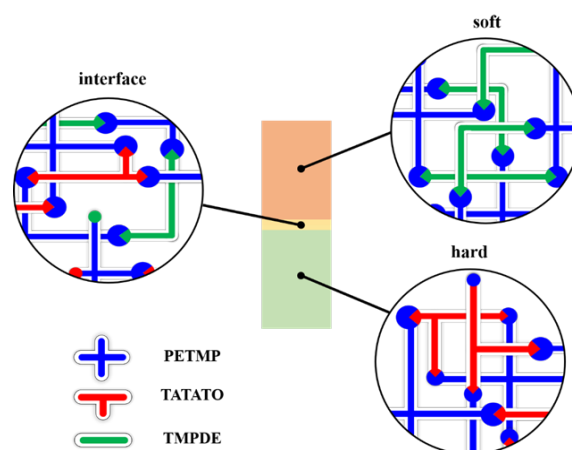


Figure 1. The structure of soft-hard alternate material

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Field Concentration in Hydrogel-Elastomer Devices

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Dielectric elastomer actuators (DEAs) are promising for many applications owing to their remarkable merits such as large deformation, fast response, high efficiency, low cost, and light weight. Recently, hydrogels have been used to activate DEAs. In these devices, hydrogels serve as the stretchable transparent electrodes and elastomers serve as the stretchable transparent dielectrics. However, the emerging of such hydrogel-elastomer devices has posed many challenges due to the distinct nature of hydrogel and elastomer. Intensive researches are taking place to learn more about hydrogel-elastomer systems in order to meet the challenges.

In this work, we study field concentration and its influences on hydrogel-elastomer devices. We fabricate a DEA by using polyacrylamide (PAAm) hydrogels containing lithium chloride (LiCl) as the electrodes and polydimethylsiloxane (PDMS) as the dielectrics. We find that most devices fail on the side of electrodes where field concentration is the strongest. We observe salting out phenomenon and local temperature increase (**Fig. 1**), as well as plasma during the experiments. We hypothesize that electric field concentrates at the edges of hydrogels, causing the surrounding air to break down. Breakdown of air produces plasma that heats up hydrogels thus leading to the salting out. We note that the breakdown of air helps dissipate energy into the air and protects the DEAs. In the end, to show that the field concentration can be useful, we demonstrate two proof-of-concept devices by taking the advantages of field concentration.

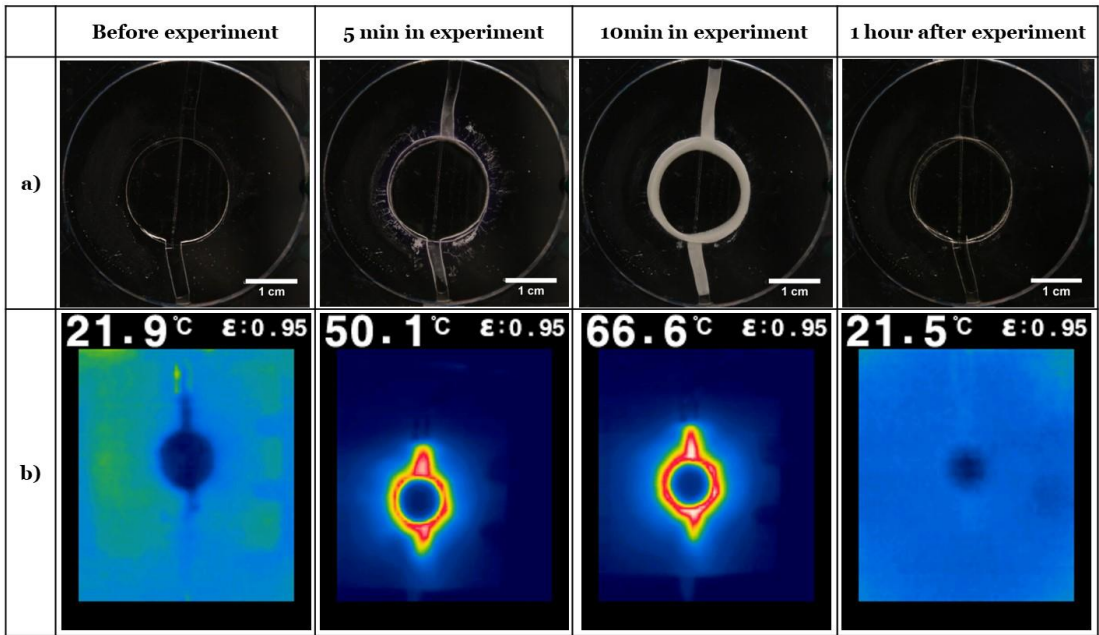


Figure 1. Salting out and localized temperature increase. a) Digital images showing the salting out evolving process of a DEA driven by PAAm hydrogels containing 8 mol/L LiCl under applied voltage that is 80% of the break down voltage with frequency fixed at 1 kHz. b) Corresponding thermal images of the DEA before experiment, 5 minutes in experiment, 10 minutes in experiment and 1 hour after experiment. Local temperature increase is observed. The highest local temperature reaches 66.6 °C after 10 minutes of experiment.

Study on self-healing and high-permittivity silicone elastomer/keratin composite materials

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Dielectric elastomers (DEs), which are often referred to as “artificial muscles”, represent an emerging and promising transducer, due to their excellent ability to have a large deformations under an applied electric field.^[1] The most obvious challenge that current elastomers face is the high driving voltages necessary to active the DEs.^[2] One effective way to overcome this shortcoming is to increase the permittivity of DEs materials.^[3] Ionic liquids (ILs), which have gained significant attention in recent years, have high permittivity and conductivity. It is therefore meaningful to apply ionic liquids to elastomers to increase their dielectric permittivity.^[4]

In this article, the high permittivity dielectric elastomer materials were prepared through the synthesis of silicone elastomers loaded with ILs. The influence of the structure and content of ILs on the material properties was discussed, and the important parameters for the given application as DE, such as dielectric permittivity, dielectric breakdown strength, gel fraction and mechanical properties, were investigated. It was found that 1-butyl-3-methylimidazolium hexafluoroantimonate (BmimSbF₆) is the most suitable IL for the dielectric elastomer material, and the permittivity of the material with 90 phr BmimSbF₆ is 318% of the pristine silicone elastomer. Although, the permittivity of elastomer materials was decreased when the temperature increased, the permittivity of the elastomer with 90 phr BmimSbF₆ (6.60) is still 320% of the pristine silicone elastomer (2.06) at 100 °C. Compared to the reference material, the mechanical properties of the materials with IL loading are not significantly changed. The gel fraction of the material decreased slightly with the increase of ionic liquid content.

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Coating with inherent sensing functionality based on dielectric elastomer

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Biofouling and barnacles accumulation on synthetic surfaces, which are exposed to the natural aqueous environment, presents serious problem in the marine industry [1]. High cost of registrations of antifouling coatings containing toxic ingredients, ecological awareness and high cost of cleaning damaged coatings, led to substantial interest in the development of coatings with sensing and self-cleaning functionality.

Current antifouling approaches and technologies include coatings with controlled release of biocides in order to detach biofouling from the surface, and systems where intentional deformation of dielectric elastomer (DE) can be employed to detach biofouling species [1, 2]. However, the detection of biofouling and barnacles on the synthetic surfaces exposed to the aqueous environment is still visual only. Hence, a need is to develop a new approach that enables more effective detection of biofouling and thus easier cleaning of fouled surfaces.

The objective of the PhD project is to fabricate a sensor based on DE, which actively and effectively detects biofouling and barnacles on the synthetic surface exposed to the aqueous environment. This sensitive surface will be made from materials, which are already used in the coating industry. The sensor will be made as a system with two compliant electrodes and intermediate silicone based DE between them, where the change of the capacitance of the sensor will indicate the presence of biofouling and barnacles on the surface of the sensor. This change of the capacitance of the sensor is caused by a change of the thickness and surface area of the DE in response to external stimuli. In order to obtain high sensitivity sensor, the choice of DE is highly important, therefore different commercially available DE are tested. First sensors are made with gold and copper electrodes, and when acceptable sensitivity of the sensor is obtained, these electrodes will be replaced with compliant electrodes based on carbon black nanoparticles which are dispersed in silicone.

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Mechanical properties and long-term stability of condensation curing silicone elastomers



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Silicone elastomers are materials well known for their good thermal and oxidation stability, flexibility, hydrophobicity, low surface energy, etc. Due to these properties, silicone elastomers found their use in many applications e.g. in electronic, medical, automotive, aerospace and other industrial fields. Nevertheless, for many of the applications, good mechanical properties are also required and due to the inherent softness of the network, silicone elastomers suffer from poor mechanical properties. Several methods to improve the mechanical properties have been developed (e.g. addition of fillers and chemical modification of the network). Nevertheless, the improvement in mechanical properties comes often together with deterioration of some of the desirable properties mentioned above.^[1] It is believed that one possible way to improve mechanical properties without influencing other desirable properties is by changing the network structure. Several studies regarding the structure-property relationship have been done by preparing so-called bimodal networks.^[2-4] Nevertheless, no data on long-term stability of such networks have been reported.

The aim of this work is to study the structure-property relationship and long-term stability of silicone elastomers. All silicone networks are prepared by condensation curing chemistry (Figure 1). The stress-strain properties of silicone elastomers with different network structures are measured by ARES-G2 rheometer over several months and mechanical instability of all prepared silicone networks is reported. Therefore, the main focus of the study is paid to the reason of the instability and to the design of silicone elastomer with well-defined and stable network structure. In order to prepare stable condensation curing silicone elastomer networks following parameters, which are found to be highly co-dependent, are considered: sample thickness, humidity, type and concentration of cross-linker.

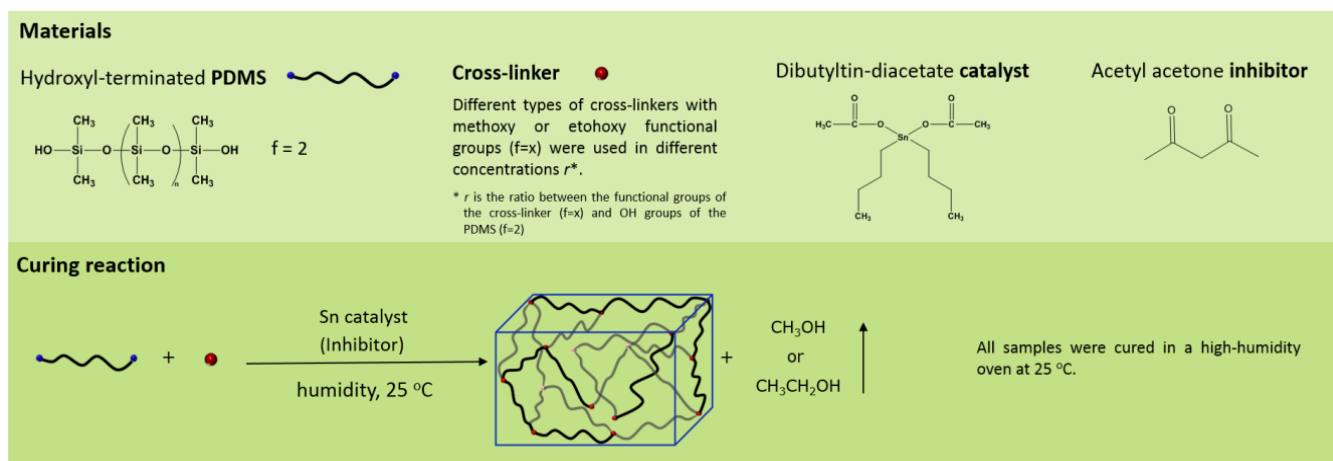


Figure 1: Chemicals and curing reaction used to synthesize condensation curing silicone elastomers.

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Stretchable conductive elastomers

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Flexible electronics have become a fast growing industry and it is the future trend of development of electronic products.¹ Stretchable conductive materials, as the key materials in the flexible electronics, can maintain a high level of electrical performance and reliability when they have large deformation.² Polydimethylsiloxane (PDMS) is one of the most utilized elastomers for flexible electronics applications due to its high efficiency and fast response.³ Multi-walled carbon nanotubes (MWCNTs), as one of the most important conductive fillers, have recently attracted a lot of attention for applications in conductive materials.⁴

In this work, a new methodology for distribution of MWCNTs in PDMS has been developed to prepare stretchable conductive elastomers, which have much higher elongations at break than comparable commercial systems. The electrical and mechanical characterization (Figure 1) shows that the materials can maintain a high conductivity under high strains without the traditionally observed loss in conductivity at high strains.

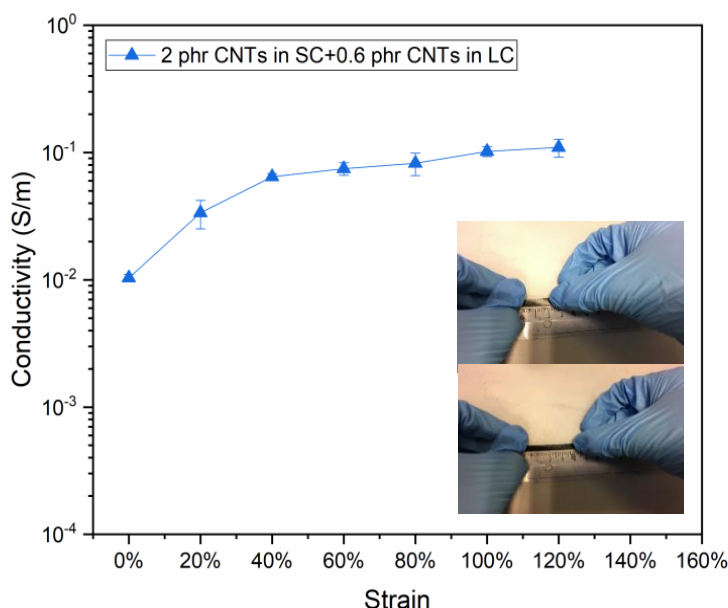


Figure 1: Conductivity of a prepared sample as a function of strain.

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Increasing selectivity of modified PES membranes through controlled pore collapse

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Polyethersulfone is a widely used ultrafiltration membrane material thank to its good film-forming and membrane-forming properties, thermal stability, chemical inertness, and mechanical strength. Polyethersulfone membranes find a range of applications in food processing [1], biomedical field [2], and water-treatment technologies [3]. To further extend the application range of these membranes, there is a strong need for control over membrane properties.

Here we demonstrate how modification of membrane surface chemistry can be used to control the extent of pore collapse and ultimately to tailor membrane properties. Commercial hollow-fiber PES membranes were activated by a heterogeneous reaction introducing benzyl chloride functionality to the surface from which surface-initiated atom transfer radical polymerization of several monomers was conducted (Figure 1) [4]. It has been shown that the graft density and chain length of the surface polymer graft can be controlled. The polymer grafts could be used for controlling the water flux and solute rejection characteristics of the membranes. The modified membranes were subsequently dried to facilitate pore collapse. The chemical nature of the grafted polymer is directly reflected in the water flux-to-rejection ratio and the extent of pore collapse. Controlled membrane pore collapse could be exploited to obtain higher rejection.

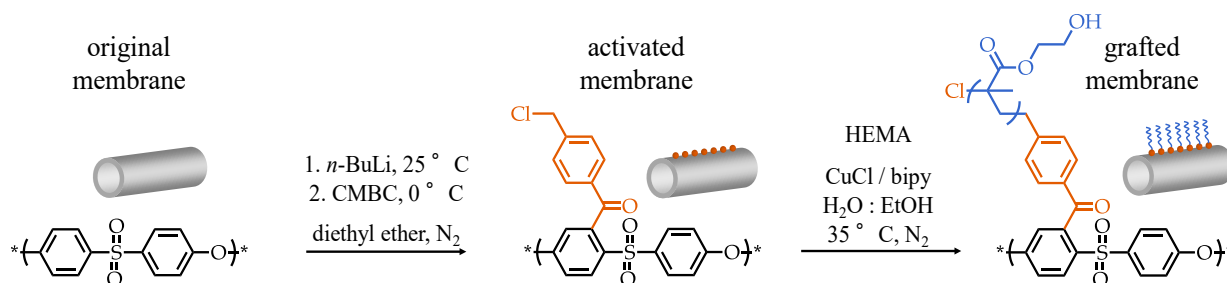


Figure 1: Activation reaction and subsequent graft polymerization of PES membrane.

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Rheological and mechanical properties of polystyrene with hydrogen bonding

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Recent work [1] shows that polystyrene can become flexible at room temperature by stretching the melt at a rate faster than the inverse Rouse time, followed by rapid quenching below the glass transition temperature (T_g). Long-lasting flexibility and good humidity resistance, combined with other advantages such as light weight and interference immunity, make this flexible polystyrene a good candidate for plastic optical fibers (POFs). However, improvements are required to prevent cracks during filament bending.

In the present work, we investigate if crack prevention can be achieved by introducing hydrogen bonding (carboxylic acid groups) into the backbone. The rheological and mechanical properties of polystyrenes with different acid group contents are studied and compared to the corresponding pure polystyrene sample. Linear viscoelastic (LVE) measurements have experimentally confirmed that all the tested samples have a similar number of entanglements per chain (Z), suggesting that the acid groups do not form (or weakly form) hydrogen bonds at temperatures above T_g . This is further confirmed by non-linear extensional behavior measured by stretching the samples in uniaxial extensional flow. However, different mechanical properties at room temperature have been observed, which may be explained by the Haward and Thackray model.[2] Finally, to further improve mechanical properties of polystyrene based polymers, different types of polystyrene ionomer will be employed for future studies.

[1] Huang et al., *ACS Macro Lett.* 7, 1126–1130 (2018)

[2] Meijer and Govaert, *Prog. Polym. Sci.* 30, 915–938 (2005)