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Silicone films by crosslinking of polymethylhydrosiloxanes with N,N-diallyl-4-nitroaniline

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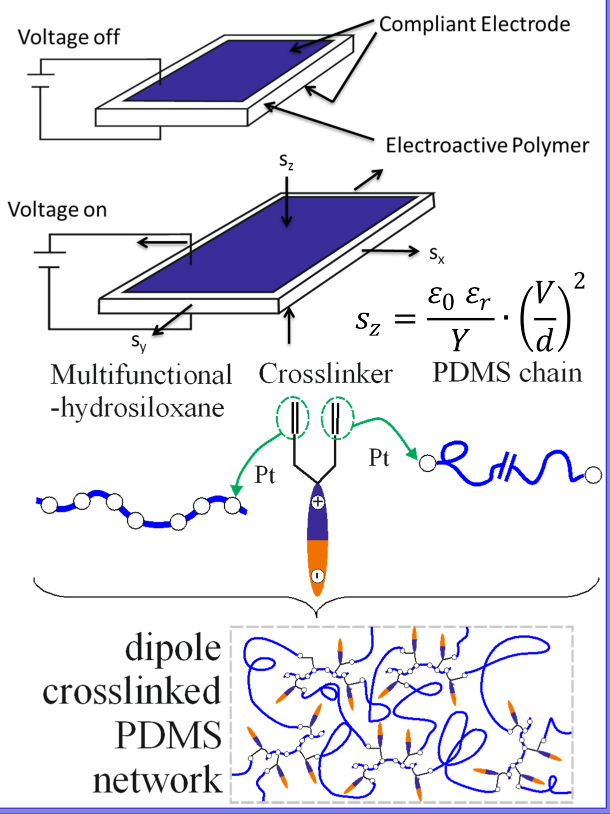
Abstract

Dielectric elastomer actuators (DEAs) enable a wide range of interesting applications since they are soft, lightweight, low-cost and have direct voltage control. However, one of the main obstacles to their wide-spread implementation is their high operating voltage, which tends to be several thousand volts. The operating voltage can be lowered by reducing the thickness, increasing the permittivity or lowering the stiffness of the elastomer. Recently, we offered a method to increase the permittivity of silicones from 3 to 6 via dipole-grafting simultaneously accompanied by significant stiffness reduction. [1] During network formation the used dipole N-allyl-N-methyl-4-nitroaniline and divinyl-terminated polydimethylsiloxane compete to bind covalently to the polymethylhydrosiloxane crosslinker. Therefore, the dipole is connected only as a side-group to the crosslinker.

Here we present a new approach using the difunctional dipole N,N-diallyl-4-nitroaniline as crosslinker for polymethylhydrosiloxanes. The Pt-catalyzed crosslinking reaction is optimized to obtain qualified silicone films with different dipole concentrations varying from 0.5 wt% to 1 wt%. The mechanical properties, the permittivity and the electromechanical properties of the films were characterized for varying nitroaniline content. For these novel elastomer materials an actuation strain of 13 % was measured at 40 V/micrometers.

Introduction / approach

- Silicones (polydimethylsiloxanes, PDMS) are widely used as electroactive polymer
- Materials' permittivity can be increased by inorganic or organic modifiers
- With organic dipoles (at high amounts) it was possible to simultaneously reduce the Young´s modulus [1]. The dipoles were bound to the crosslinker as side groups.
- In this work we want to study the influence of the dipole if they are a part of the polymer chain and bound at two positions.
- Therefore we used the difunctional dipole as a crosslinker
- The general idea behind:
    - Hydrosiloxane groups of the high molecular PDMS and the multifunctional copolymer allow the usage of difunctional dipoles as crosslinker
    - Dipoles are incorporated as a network point
    - Only small amounts of dipole needed, should result in low dielectric loss



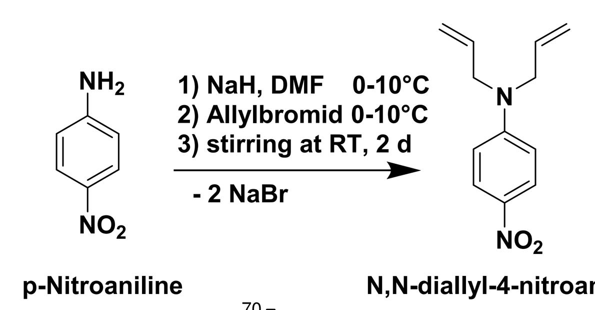
Film formation

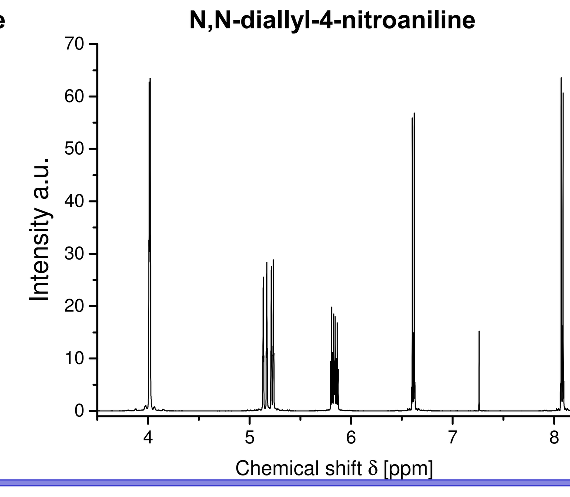
Four solutions are prepared with $CHCl_3$ as solvent: **A** (DMS-H25, SiO_2), **B** (HMS-301), **C** (dipole crosslinker), **D** (kat.). Solutions **A** till **D** are required to form the network by solvent-casting in a ducted metal frame (PTFE bottom) covered with a perforated metal plate. After solvent evaporation over night, the films were cured at 120° C for 30 minutes.

DMS-H25: 17.200 g/mole, f = 2

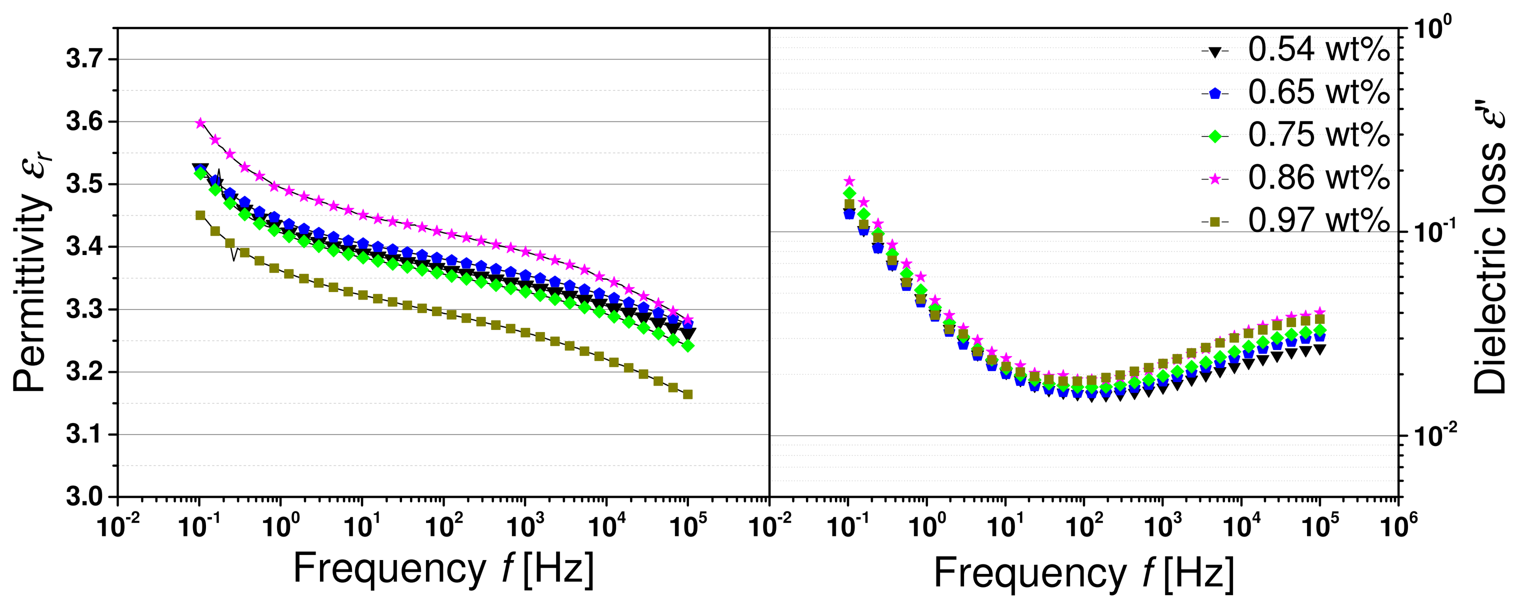
HMS-301 : 1.950 g/mole, f = 7.51

Dipole synthesis





Electrical properties



Permittivity

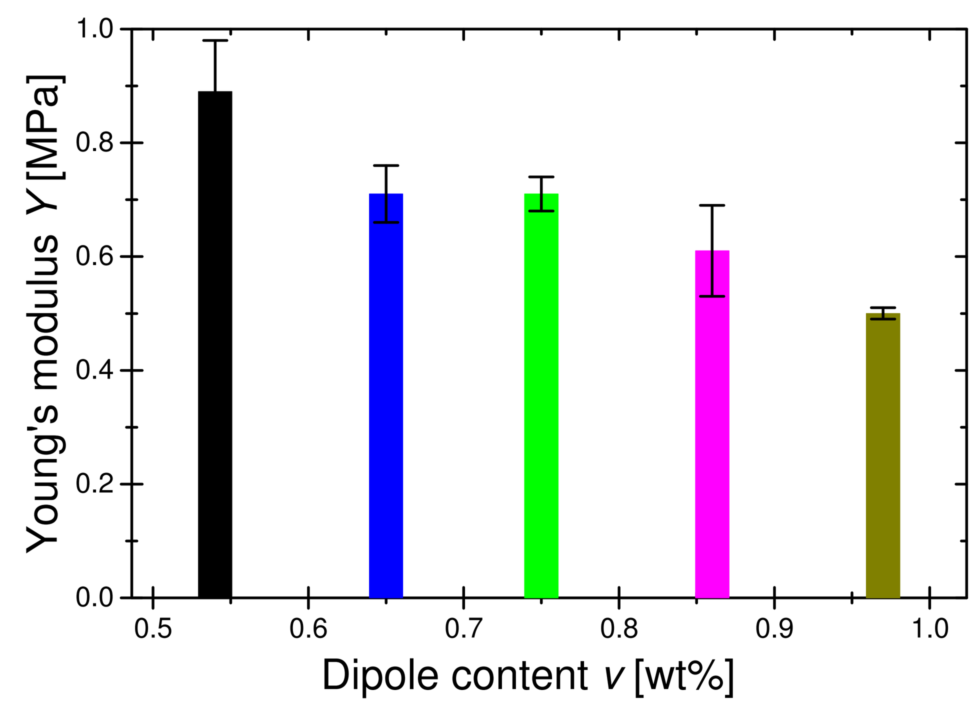
- Permittivity slightly enhanced compared to pure PDMS-networks ($\varepsilon_r \approx 3$ @ 1 kHz)
- Increase of ε_r due to dipole presence

Dielectric loss

- Losses higher then in pure PDMS-networks
- All films show comparable dielectric losses

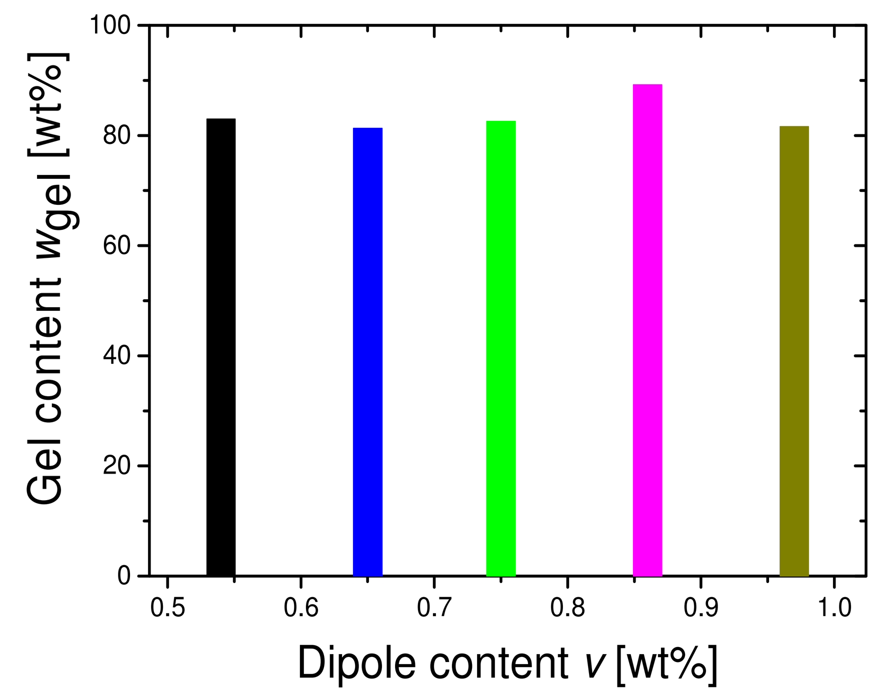
Mechanical properties

Influence of dipole content on Y-modulus



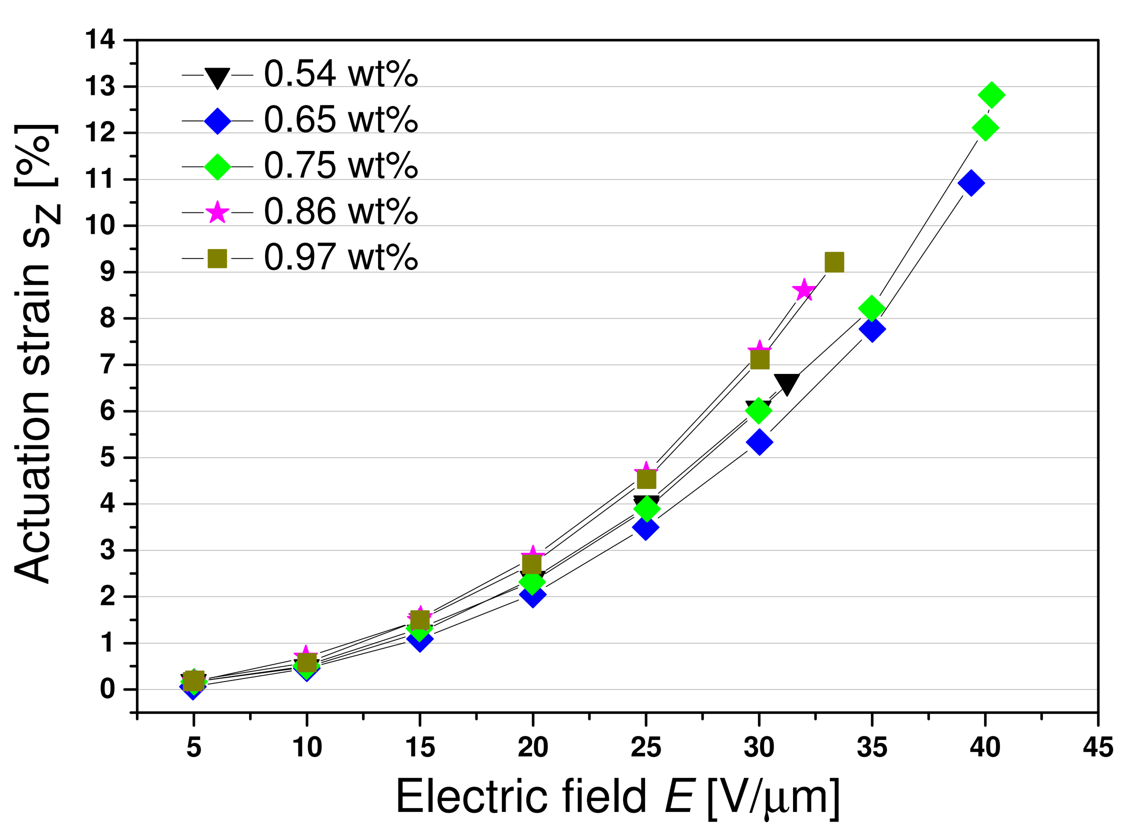
- Y-modulus decreases with increasing dipole content
- Lowest Young´s modulus at 0.5 MPa for 0.97 wt%

Influence of dipole content on gel content



- Gel content in the same region between 80 and 90 wt%
- Dipole modification slightly reduces the gel content compared with standard silicone systems

Actuation measurement

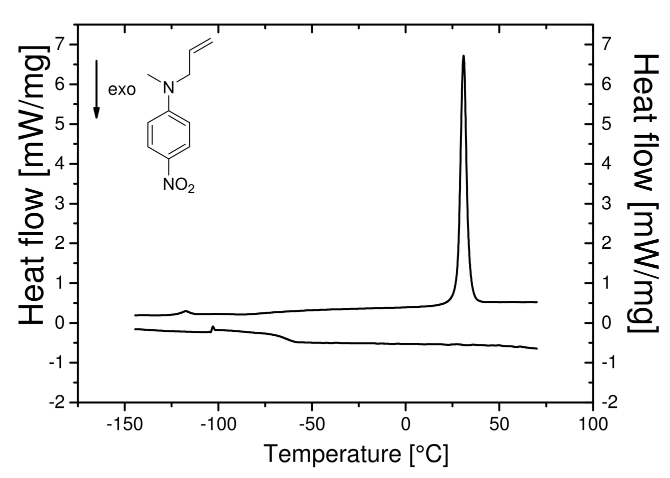


- Actuation up to 13 % at 40 V/µm with 0.75 wt% dipole content
- Highest sensitivity β for films with 0.86 wt% dipole content
- Breakdown field strength E_{BD} was measured under actuation

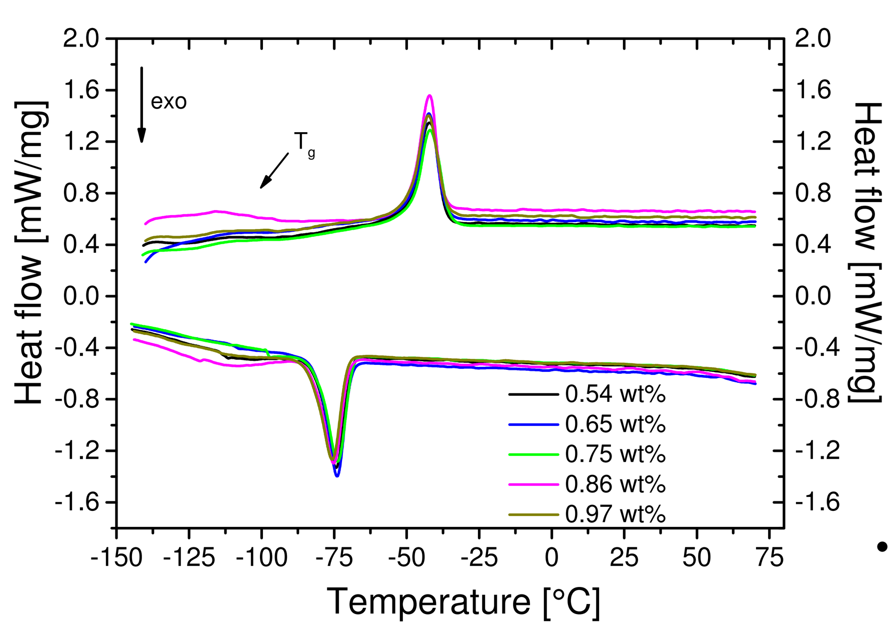
$$s_z = \frac{\varepsilon_0\,\varepsilon_r}{Y}\cdot\left(\frac{V}{d}\right)^2 = \beta\cdot E^2$$

Thermal properties

Differential scanning calorimetry



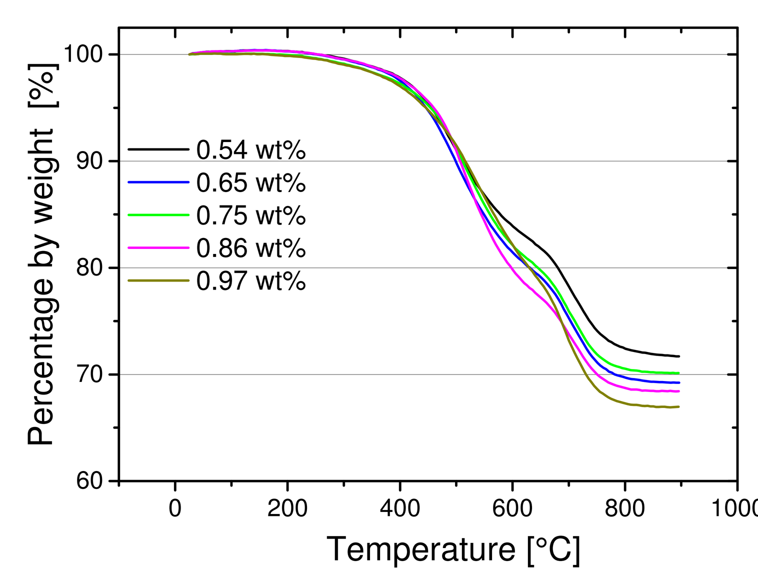
- Melting point of dipole at 30°C, which is not detectable in the silicone films



	Sample	ϑ [°C]	Area [J/g]
Cooling	0.54 wt%	-74.4	-18.8
	0.65 wt%	-74.0	-20.1
	0.75 wt%	-73.8	-19.6
	0.86 wt%	-75.2	-18.2
	0.97 wt%	-75.7	-19.8
	Dip	T_g -63.7	
Heating	0.54 wt%	-42.2	19.4
	0.65 wt%	-42.4	20.1
	0.75 wt%	-42.0	20.3
	0.86 wt%	-42.1	20.8
	0.97 wt%	-42.5	20.3
	Dip	30.9	76.6

- Only minimal changes of melt- and crystallization peaks

Thermogravimetric analysis



- At 300°C almost 97 % of the masses remains

Conclusions

- Silicon films can be obtained from hydrosiloxanes by crosslinking with difunctional dipoles
- The dipole is connected completely to the silicone network, no crystals of dipole observed in the silicone films
- The dipole content is less than 1% to achieve full crosslinking
- Permittivity between 3.2 and 3.4 @ 1 kHz
- Low dielectric loss was found
- Young´s modulus between 0.9 MPa to 0.5 MPa

References

[1] B. Kussmaul *et al.*; *Adv. Funct. Mater.* **2011** *21*, 4589-4594.

Acknowledgments

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