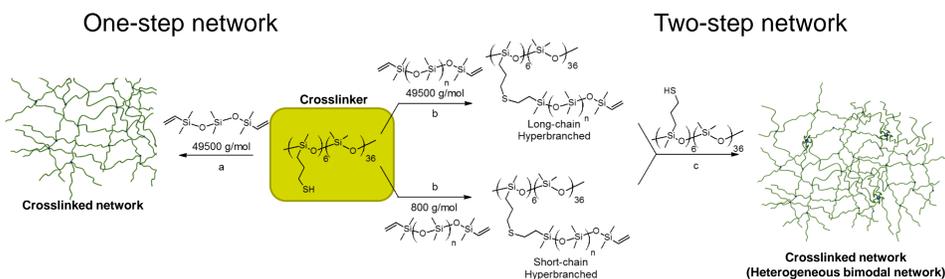


Introduction

In silicone industries, the majority of vinyl terminated silicones that are cured at low temperatures uses platinum catalyzed addition reactions. Only a few silicone formulations can be cured through UV curing, and most of these UV curable silicones still use platinum for additional addition crosslinking reactions¹. The major drawbacks of platinum catalyzed crosslinking of silicones are the highly priced noble metal catalyst used in the crosslinking reaction as well as poisoning of the catalyst by compounds containing nitrogen, sulfur, phosphorus and tin. Studies have been done extensively on UV curing of acrylic silicones² or classical condensation curing by UV light³, but very few examples on vinyl terminated silicones are available in the literature⁴.

This work aims at photoinitiated thiol-ene cross-linking of high molecular weight PDMS prepolymers as a pathway to novel soft PDMS networks. The approach permits controlled distribution of fillers in the network, which has been applied with a multi walled carbon nanotube (MWCNT) to provide high-capacitance non-conductive elastomers. Such materials would find applications in dielectric electroactive polymers for actuators, generators or sensors.

Preparation UV-cured PDMS



Scheme 1. One-step or two-step UV curing of PDMS using DMPA as photoinitiator, $h\nu$ ($\lambda=365$ nm); a) direct crosslinking; b,c) hyperbranching with excess of α,ω -vinyl-PDMS. Combination of the hyperbranched intermediates in the second step of the two-step procedure resulted in a fast and efficient network formation.

Comparison of One-step vs. Two-step procedure

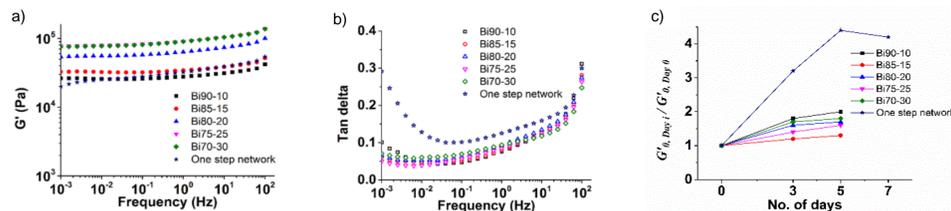
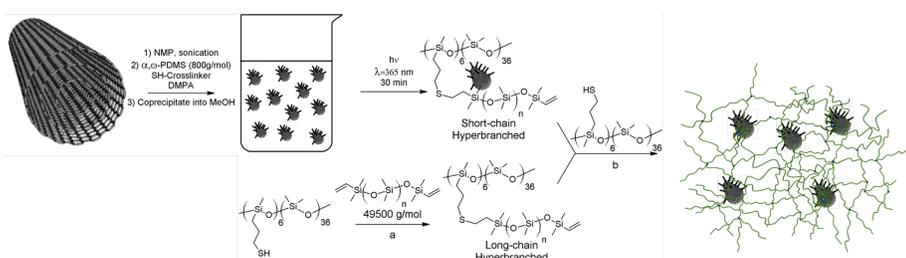


Figure 1. a) Storage moduli (G') (a) and tan delta (b) of the fully cured two-step networks compared to the one-step network as a function of frequency. Bi-xx-yy refers to the two-step systems with a ratio of xx hyperbranched high molecular weight PDMS to yy hyperbranched low molecular weight PDMS. Measurements are performed at room temperature. c) Development in storage moduli (G') for the respective networks relative to the initially observed storage modulus measured immediately after the curing reaction and after storage at RT in the dark for up to 5 or 7 days.

Two-step network formation:

1. Efficient procedure for UV curing without platinum
2. Lower viscous loss and no postcuring compared to the one-step procedure
3. Softer PDMS networks with lower storage moduli were directly obtained

Spatially controlled distribution of MWCNT in PDMS



Scheme 2. Two-step UV curing of PDMS using DMPA as photoinitiator, $h\nu$ ($\lambda=365$ nm); In the first step a short chain hyperbranched system is formed around the MWCNT. As for the non-filled system a hyperbranched long-chain system is prepared with excess of α,ω -vinyl-PDMS. Combination of the hyperbranched short-chain MWCNT structure with the long-chain hyperbranched intermediate resulted in a preparation of a network with distributed MWCNT domains.

Table 1. Composition of the filled PDMS elastomers.

Sample name	MWCNT wt%	Treated fumed silica wt%
HPD_0	0	25
HPD_0.33	0.33	25
HPD_0.66	0.66	25
HPD_1	1	25

Characterization of filled systems

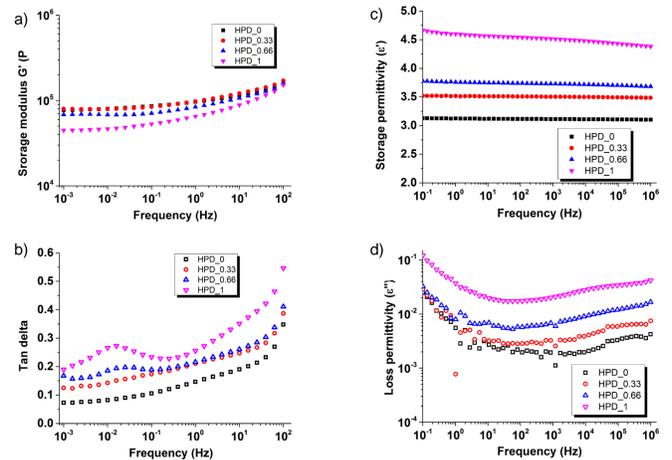


Figure 3. Rheological characterization (a,b); dielectric relaxation spectroscopy (c,d); a) storage modulus (G') and b) Tan delta as function of frequency for treated fumed silica filled PDMS networks with and without modified MWCNT at 23°C. a) storage permittivity and b) loss permittivity as a function of frequency for PDMS composites at 23 °C.

Conductivity and breakdown

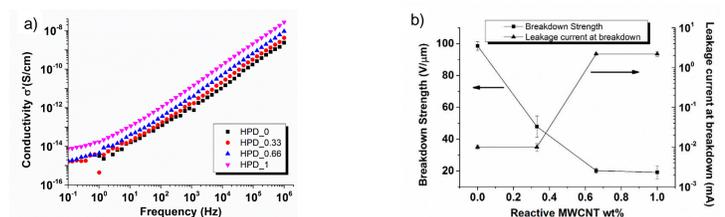


Figure 4. a) Variation of AC conductivities as a function of frequency for PDMS composites at 23 °C. b) Variation of breakdown strength and leakage current of the PDMS composites as a function of modified MWCNT content.

Temperature effects

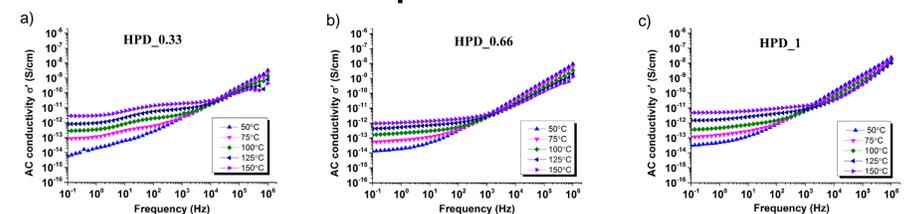


Figure 5. Temperature dependent AC conductivities of (a) HPD_0.33 (b) HPD_0.66 (c) HPD_1.

Results and discussion

The two methods investigated from Scheme 1 were found to be possible pathways to UV crosslinkable PDMS without the use of noble metals. The two-step reaction enabled straightforward preparation of soft networks with low viscous losses and no postcuring. Additionally, the two-step approach opens up for possible inclusion of fillers in the inner network, which is a very attractive approach to include high-permittivity fillers without obtaining conductive composites. A modified procedure incorporating dispersion and coprecipitation of a MWCNT together with the short-chain PDMS was developed and used for preparation of a filled elastomer as shown in Scheme 2. Elastomers with a varied content of MWCNT were prepared by variation of the amount of inner network relative to the outer network. The prepared composites fulfill several of the requirements for DEAP materials, including higher permittivity and low viscous losses (Figure 3). The elastomers were found to be non-conductive at RT above what is normally considered the percolation threshold (Figure 4). However, increased leakage current and electrical breakdown at lower voltage were observed above 0.33 wt% MWCNT even though the samples were found to be non-conductive in the entire frequency range. An investigation of the conductivity as a function of temperature (Figure 5) shows that the semiconducting properties of the MWCNT might be the source of the premature breakdown contrary to what would be expected from the RT conductivity.

Conclusion

1. Two-step procedure permits distribution of fillers in the network
2. Non-conductive elastomers with up to 1 wt% MWCNT in PDMS could be prepared
3. High permittivity was observed with no conductivity
4. Breakdown > 40 V/ μ m for up to 0.33 wt% MWCNT
5. Lower breakdown voltages may be a result of semiconducting MWCNT and heating during analysis

Acknowledgements

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