Challenges of thin silicone condensation curing films with well-defined structure

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Abstract
In this study, preparation of thin films (~100µm) of condensation-curing silicones is investigated. It is found that behavior of typical condensation curing system consisting of OH terminated poly(dimethylsiloxane) (OH-PDMS), tin catalyst and methyltrimethoxysilane (MTMS) or tetraethoxysilane (TEOS) cross-linker is highly dependent on the sample thickness. High volatility of the cross-linkers that becomes enhanced with decreasing sample thickness is reported. The high volatility does not allowed for proper curing of thin silicone films, even though the cross-linker is used in excess. In addition, reliability and reproducibility of such system becomes an issue.

Introduction
Silicone elastomers are materials known for good thermal and oxidation stability, flexibility, hydrophobicity, low surface energy, etc. This makes them the first choice for many applications in electronic, medical, automobile, aerospace and many other industrial fields. Nevertheless, the use of silicone elastomers is limited by their rather poor mechanical properties. The improvement of mechanical properties by addition of fillers or by chemical modification comes often together with deterioration of some of the properties mentioned above [1]. One 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 in addition curing silicones [2, 3]. Nevertheless, not much work has been done in the more economically friendly, room temperature curing condensation type of silicone elastomers [4]. In addition, no study was conducted with respect to the long-term properties of the networks. Therefore, preparation of condensation curing type of silicone elastomers with well-defined structure and stable properties over time remains a challenge, especially when thin films are required.

Materials & Methods
Silicone elastomers were prepared by condensation curing reaction between methoxy groups of the cross-linker and OH groups of the OH terminated PDMS in a high humidity oven at 25°C (Figure 1). The stoichiometric ration between functional groups of MTMS cross-linker (f = 3) and OH-PDMS (f = 2) was kept equal to r = 5.

Results and Discussion
The influence of sample thickness on condensation curing reaction of silicone elastomers has been investigated. From Figures 2 and 3 can be see that weight loss of the sample over time is highly dependent on the sample thickness. The weight loss during condensation curing reaction is a typical feature caused by alcohol release (Figure 1). Nevertheless, if only alcohol (in this case methanol) and eventually the catalyst would be released from the system, no difference in the final weight loss percentage of the samples should be seen, because the composition stays the same for all tested thicknesses. In addition, the films of thickness ≤ 0.6 mm are not cured.
and samples with thickness ≥ 1.5 mm remain sticky on the surface, if methyltrimethoxysilane (MTMS) from new bottle is used (Figure 2). This signifies uncompleted curing of the samples even thought, the MTMS was used in high excess (r=5).

The evaporation is significantly decreased if old bottle of MTMS product is used as can be seen in Figure 3. Samples of all thicknesses were cured within few hours, without leaving the surface sticky. This is probably due to partial hydrolyzation and subsequent condensation of the MTMS, resulting to a mixture of hydrolysis product, which are less volatile compare to pure MTMS and therefore are able to cross-link the system. This means that attention has to be paid if MTMS and TEOS cross-linkers are used for condensation curing of the silicone elastomer. As due to the high volatility of the cross-linkers, the system is sensitive to the thickness of the sample, time required for the mixing of the components and temperature and humidity during the sample preparation. In addition, the cross-linkers are prone to hydrolyzation, which limits the reproducibility of the curing reaction.

Figure 4 summarize long term stability of the silicone networks cross-linked by partially prehydrolyzed MTMS represented by Young’s modulus and elongation at break. The measurements were done using ARES-G2 rheometer. It can be see that both, elongation at the break and the Young’s modulus are not stable over time.

Figure 3: Weight loss (%) of the samples consisting of C2T, MTMS (old bottle, 2.55 wt%) and dibutyltin diacetate (1.14 wt%) over time. Thickness of the samples was varied from 0.2 to 5.5 mm.

The results above indicate high volatility of MTMS cross-linker, if it is used in high purity without any trace of hydrolyzation. Therefore, the weight loss presented in Figure 2 is a combination of the MTMS evaporation, methanol release and eventually catalyst evaporation. Such cross-linker is then not suitable for condensation curing, especially if thin films are required. The same features were observed if tetraethoxysilane (TEOS) was used as the cross-linker.

Figure 2: Weight loss (%) of the samples consisting of C2T, MTMS (new bottle, 2.57 wt%) and dibutyltin diacetate (1.14 wt%) over time. Thickness of the samples was varied from 0.2 to 5.5 mm.

The volatility of MTMS is decreased if the MTMS used as the cross-linker.

Figure 4: Long-term properties of silicone elastomer (thickness 100 µm) consisting of C2T, MTMS (old bottle, r=5) and dibutyltin diacetate (~1 wt%) represented by elongation at break (%) and Young’s modulus (MPa).

Conclusion
For preparation of thin condensation curing silicone elastomer films, special attention has to be paid to the choice of the cross-linker. Cross-linkers, typically used for condensation curing of silicone elastomers, MTMS and TEOS, suffer from high volatility and are therefore unable to take part in the curing reaction if the required film thickness decrease under certain level. The volatility is decreased if the cross-linkers mentioned above are partly pre-hydrolyzed. Nevertheless, even though partly hydrolyzed MTMS allowed the curing of thin silicone elastomer layer, the mechanical properties of the film are not stable over time. Therefore, different, more stable cross-linkers have to be considered in the future.

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References