

UV-Activated Hydrosilation Reaction for Silicone Polymer Crosslinking

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ABSTRACT: In this article hydrosilation was employed to achieve a fully cured three-dimensional silicone network. The UV-activated hydrosilation reaction was investigated focusing on the curing conditions and their relationships to physical properties. After finding the optimum catalyst concentration, it was observed that by decreasing the molecular weight of the vinyl oligomer a slight increase of the T_g value was achieved together with a complete suppression of the T_m . It was possible to fully cure samples up to 4 cm of thickness. The dark curing process was evaluated by FTIR analyses and it was evidenced an important increase on dark-polymerization, which is dependent on the length of the UV-irradiation time. This result shows the versatility of UV-curing technique for silicone network formation. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Silicone materials have been produced commercially since the beginning of the 1940s. Nowadays they are used in many applications as for example in construction building, electrical transportation, aerospace, and cosmetics industries.^{1,2} Silicone polymers present a “polysiloxanic” backbone made of sequences of $-\text{[SiR}_2\text{-O-]}_n-$ where R indicates functional groups such as methyl, vinyl, phenyl or per-fluoropropyl. These substituents can be easily varied and modulated in order to obtain silicone rubbers with different properties.

Silicone polymers can be cured following different methods, depending if a room-temperature vulcanization (RTV silicones) or a high-temperature vulcanization (HTV silicone) reaction is performed. Most often a high-temperature vulcanization is performed and it can be achieved mainly with two different methods: A vulcanization reaction using peroxides, in which curing reaction occurs via a radical chain polymerization reaction which is started and promoted by homolytic cleavage of organic peroxides. The generated radicals can attack the vinyl $\text{C}=\text{C}$ double bond with the formation of chemical crosslinks between the polymeric chains.³

And a vulcanization reaction using catalyst, in which curing reaction is similar to a polymerization reaction which is activated by the platinum catalysts. It is known as hydrosilation reaction and occurs between vinyl and silane groups present on different silicone chains. This reaction is catalyzed by the presence of platinum compounds.⁴

Hydrosilation is therefore the addition of a Si-H bond across a $\text{C}=\text{C}$ double bond. In general this process has become the method of choice for synthesizing organofunctional silicon compounds. The reaction is complex and it is not a simple matter to make really effective use of it. A number of products have been obtained by the reaction of silane with olefins.

Hydrosilation was first reported in 1947 by Sommer⁵ in the reaction between trichlorosilane and 1-octene in the presence of acetyl peroxide. Later in 1957 Speier⁶ reported hexachloroplatinic acid as a very efficient catalyst; this discovery prompted a wide and common application by both academic and industrial synthetic chemists.

Hydrosilation is at once a fundamental and elegant method and has been exploited toward myriad organosilicon and other related silicon compounds.^{7,8}

Scientific literature in the last decades, provides a number of surveys of hydrosilation reactions or particular aspects of such processes; these include general reviews, chapters, or books.^{9–17}

Although platinum complex and many others are useful as catalysts in the process for accelerating the thermally activated addition reaction between the compounds containing silicone-bonded hydrogen and compounds containing aliphatic unsaturations, a UV or visible radiation activated addition reaction between these compounds is much less common and rarely described.

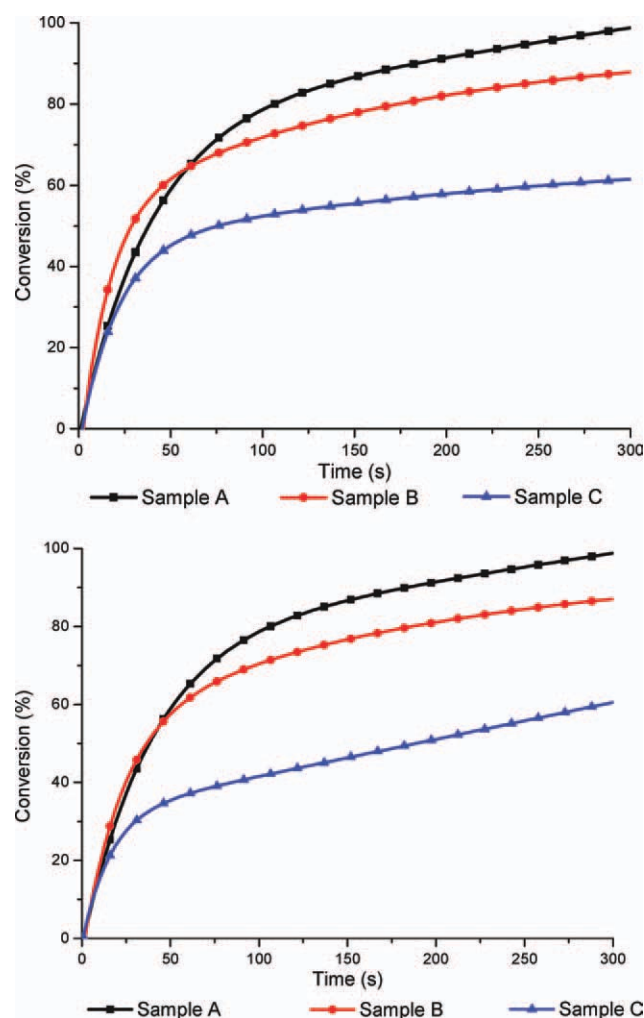


Figure 2. Silane conversion curve (peak centered at 2160 cm^{-1}) as a function of irradiation time for the formulations containing the vinyl oligomer A (molecular weight 17,200, curve \square), oligomer B (molecular weight 6000, curve Δ) and oligomer C (molecular weight 800, curve \circ). (a) Catalyst content 500 ppm. (b) Catalyst content 1000 ppm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight between two neighbor crosslinks) which could hindered the diffusion of the growing polymeric chains.

To evaluate the effect of the catalyst content, the same formulations were cured in the presence of 1000 ppm of Pt-catalyst. It was evident that the increase of catalyst content did not significantly enhance the conversion rate or final conversion, which

are comparable with the values recorded for the same formulations containing 500 ppm of Pt-catalyst [see curve of Figure 2(b) and data reported in Table I]. By decreasing the Pt-catalyst content below 500 ppm it was not possible to achieve a fully cured tack-free sample. Therefore there is a lower catalyst content below which the curing process is not efficient anymore. This behavior is similar to what was observed previously in literature.¹⁹

It is important to underline that the Pt-catalyst is the same for thermal-activated hydrosilation reaction. Performing control experiments with the same model system and the same catalyst content (500 ppm), we observed that the thermal reaction is much slower than the photoactivated reaction. Comparable SiH conversion values were achieved by thermal treatment at 80°C for 30 min with respect to UV-curing for 5 min (data not reported). This is an important advantage since there could be energy saving and enhancement on rate of productivity by using UV-activated hydrosilation reaction.

Cured materials of about $50\ \mu\text{m}$ thickness with the different formulations containing 500 ppm of catalyst were achieved by irradiating with UV-light for 5 min. It was observed that the gel content decreased by increasing the molecular weight of the vinyl oligomer (data reported in Table I). The cured materials obtained by using the vinyl oligomer with the higher molecular weight (oligomer A) showed a gel content of 74%. By using the oligomer B the gel content of cured material slightly increased to 78%. Complete insoluble cured material was obtained with a gel content of 99% by using the vinyl oligomer with the lower molecular weight (oligomer C with a molecular weight of 800 g/mol). It seems clear that by increasing the crosslinking density, a tight crosslinked polysiloxane network completely insoluble is achieved and that increasing the molecular weight will decrease the crosslink probability with a decrease of crosslinked material. When using the lower molecular weight the crosslinking density increased with an increase on T_g and of a fully cured silicone is achieved.

The glass transition temperature was determined by DSC analysis for all the cured samples. The DSC curves are reported in Figure 3, respectively for the system cured with the vinyl oligomer with higher molecular weight (oligomer A, curve A), with the intermediate molecular weight (oligomer B, curve B) and finally with the lower molecular weight (oligomer C, curve C).

It was also observed that by decreasing the molecular weight of the vinyl oligomer there is an increase of the T_g value, that

Table I. Properties of UV-Cured Materials

Sample	M_n of vinyl oligomer	Conversion (%) ^a		Gel content (%) ^b	T_g ($^\circ\text{C}$) ^c	T_m ($^\circ\text{C}$) ^c
		500 ppm	1000 ppm			
Formulation A	17,200	98	98	74	-130	-50
Formulation B	6000	78	80	78	-120	-53
Formulation C	800	51	53	99	-110	-

^aDetermined by RT-FTIR analyses after irradiation time of 5 min, ^bDetermined after 24 h extraction in chloroform., ^cDetermined by DSC analyses.

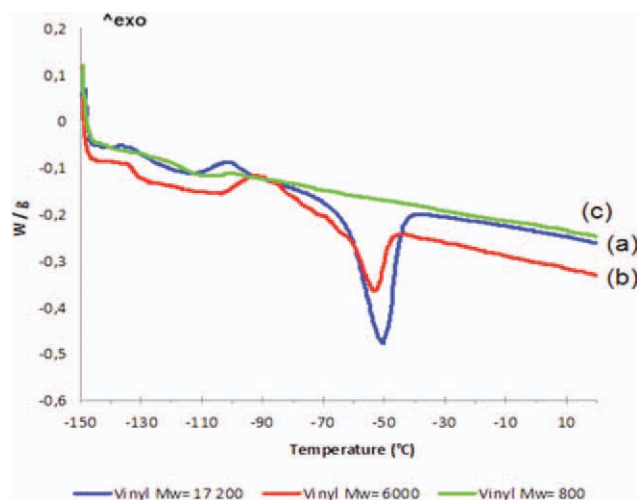


Figure 3. DSC Curves for cured materials obtained from the 1 : 1 equimolar mixture PDMS-V/MH-PDMS obtained with the vinyl oligomer with higher molecular weight (curve A), with the intermediate molecular weight (curve B) and with the lower molecular weight (curve C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shifts from -130°C for the cured material obtained in the presence of the vinyl oligomer with the higher molecular weight, up to -110°C when the vinyl oligomer with lower molecular weight (M_w of 800 g/mol) is used. Also a decrease of the crystallinity becomes evident by decreasing the molecular weight of the vinyl oligomer; a complete disappearance of the crystallinity is observed when the vinyl oligomer with lowest molecular weight is used (oligomer C).

The T_g increase is in agreement with the FTIR data showing a decrease of SiH group consumption by decreasing the molecular weight, which was explained on the basis of the increased cross-

linking density due to the higher number of reactive groups present on oligomer C. In fact it is very well known that by increasing the crosslinking density there is an extension of the elastic modulus to higher temperature with a consequent shifting to higher temperature of the viscoelastic glass transition. Furthermore by shortening the distance between two crosslinks a lower mobility of the chain-ends is induced, so that constraints are too high to allow enough mobility which is needed to get the necessary chain-folding for the crystalline structure formation. As a final result the cured materials obtained by using the vinyl oligomer with the lower molecular weight is characterized by higher T_g values, higher mechanical performances and absence of any crystallinity.

These results showed that this UV-curable systems are versatile and that it is possible to prepare materials characterized by different properties changing the molecular weight of the starting UV-curable components.

Curing into Depth

On the basis of the preliminary investigations we selected to cure a 1 : 1 equimolar mixture model formulation of PDMS-V/MH-PDMS by using the vinyl oligomer with the lower molecular weight (oligomer C, molecular weight 800 q/mol and vinyl- eq/kg 2.4–2.9) and adding an actual content of Pt-catalyst of 500 ppm. Samples were prepared in plastic molds with a thickness ranging from 1 to 4 cm. Cured materials were achieved after 5 min of irradiation.

The ATR spectra recorded on the nonincident side (bottom part) of the formulations after 5 min of irradiation are reported in Figure 4. For all samples (with 1–4 cm in thickness) a certain residual amount of SiH is always evident whereas the residual amount of SiH increase with the sample thickness (peak intensity increases). Nevertheless all the investigated thick samples were tack-free and completely insoluble with a gel content value around 98–99%.

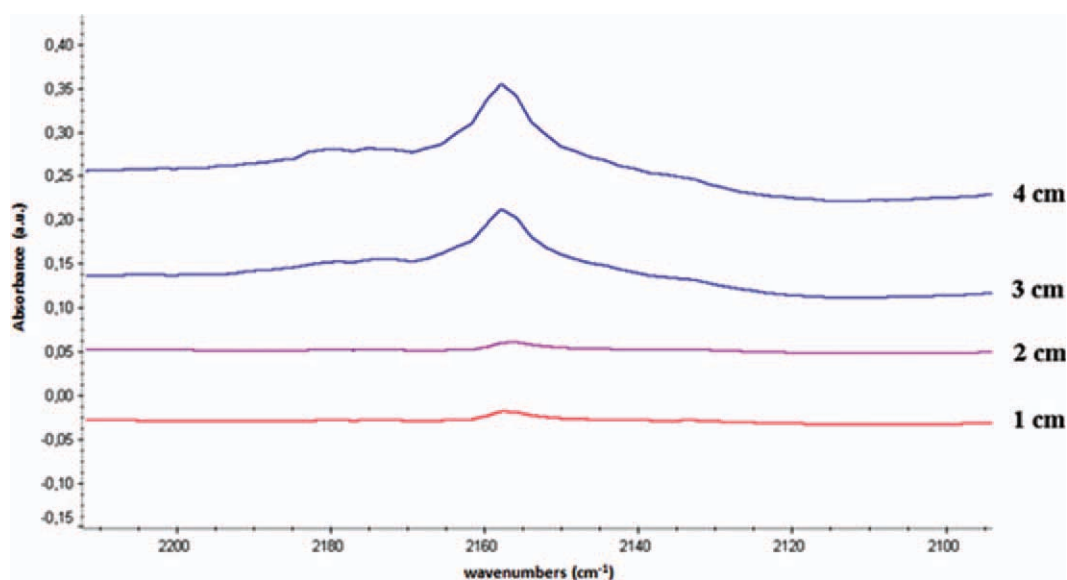


Figure 4. ATR spectra recorded on the non-incident side (bottom part) of the 1 : 1 equimolar mixture PDMS-V(Oligomer C)/MH-PDMS after 5 min of irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

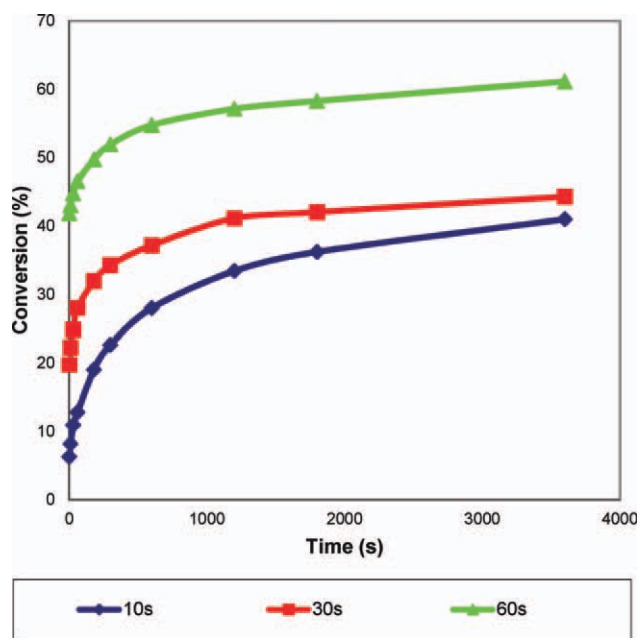


Figure 5. Evaluation of dark-curing after different time of UV-irradiation of the 1 : 1 equimolar mixture PDMS-V(Oligomer C)/MH-PDMS. Sample thickness 50 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These data are particularly interesting for UV-curing process since in the classical UV-initiation polymerization there is a well known thickness effect with a strong decrease of conversion by increasing thickness of photocurable formulation. As a matter of fact in the classical UV-induced polymerization reaction the thickness limit is very low (usually homogeneous curing are achieved for coatings of about 50–100 μm). Because of the occurrence of a gradient in intensity of UV with increase of the penetration depth, UV-curing is usually applied only for thin coatings. The possibility to achieve a thick cured material must be explained with a different curing process, which could probably involve at the same time an homogeneous and a heterogeneous catalytic mechanism, as described below on the basis of the literature data.

Evaluation of Dark-Curing Process

One important advantage of the UV-curing technique is that the crosslinking reaction can be triggered by a short UV-irradiation and it will further proceed slowly in the dark.

In order to evaluate the extent of the dark curing process, a mixture of PDMS-V (oligomer C with the lower molecular weight) and MH-PDMS with 500 ppm of Pt catalyst was investigated by RT-FTIR. The proceeding of dark curing was followed as a function of the conversion of the Si–H peak during time, after a short irradiation induction. The thickness of the sample is about 50 μm . The results are reported in Figure 5 for the formulations previously UV-irradiated respectively for 10, 30, and 60 s.

A significant increase of SiH conversion in the dark was evidenced as a function of the length of UV-irradiation. These data are in agreement with the literature data²² and show that it

is possible to achieve high conversion by a very short irradiation time and a relatively short dark postcuring.

The data reported in literature²² correlated the results of hydrosilation reaction and the spectral changes which accompanied irradiation of $\text{Pt}(\text{acac})_2$ in the presence of Et_3SiH or $\text{Et}_3\text{Si}(\text{-vinyl})$, and indicated that the irradiation time required to generate the active hydrosilation catalyst correspond to the time required for essential complete disappearance of the long-wavelength UV absorption band of the $\text{Pt}(\text{acac})_2$ and for the formation and destruction of primary photoproduct detected both by UV- and $^1\text{H-NMR}$ spectroscopy. However, the complete photodecomposition of $\text{Pt}(\text{acac})_2$ to liberate both ligands and form colloidal platinum did not occur during this brief irradiation period. These observations made postulate that short period of irradiation resulting in the formation of homogeneous hydrosilation catalyst which could be slowly converted to a less active heterogeneous catalyst similar to that formed upon thermal decomposition of $\text{Pt}(\text{acac})_2$. The heterogeneous catalyst was supposed to be the one responsible of the proceeding of the reaction in the dark as well as in depth, achieving thick cross-linked materials.

CONCLUSIONS

In this article hydrosilation was employed as an important way to achieve a fully cured three-dimensional silicone network. The UV-activated hydrosilation reaction was investigated focusing the attention on the curing conditions and the structure properties relationships. An equimolar amount of Polydimethylsiloxane vinyl dimethylsiloxane terminated (PDMS-V) with different molecular weight and a Polymethylhydrosiloxane trimethylsiloxane terminated (MH-PDMS) were mixed and the photocuring process investigated by varying the Pt-catalyst content between 500 and 1000 ppm. It was shown that by increasing the catalyst concentration there is not any significant improvement both in the rate of photopolymerization or final conversion, while decreasing the catalyst content below 500 ppm did not allowed to get a fully cured material. The optimum catalyst concentration was therefore set at 500 ppm. By decreasing the molecular weight of the vinyl oligomer it was shown a slight increase of the T_g value and a complete suppression of the T_m . The T_g increase was attributed to an increase of crosslinking density by using the vinyl oligomer with the lower molecular weight and therefore a higher vinyl functionality. Furthermore, the lower mobility of the pendant chains did not allow the requested chain-folding for polymer-crystals formation.

It was possible to cure successfully 4 cm thick samples. All the thick samples were completely insoluble. The dark curing process was also evaluated by FTIR analyses and it was evidenced an important increase on dark-polymerization, which is also dependent on the length of the UV-irradiation time. Both these results are in agreement with the data previously reported in literature which suggest that with a short period of irradiation it can be induced the formation of homogeneous hydrosilation catalyst that is slowly converted to a less active heterogeneous catalyst acting either in depth and/or in the dark. The reported results of achievement of thick cured silicone materials is

therefore of high interest since this photocured silicones could be made both for thin film as well as for bulk applications. In conclusion we have shown the important versatility of UV-curing for silicone network formation. We have demonstrated the possibility to vary the properties of the materials by ranging the starting vinyl oligomer molecular weight. Highly UV-crosslinked silicones could be achieved with higher rate of polymerization, therefore with a reduction of energy consumption and enhancement of productivity.

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