

Cross-linking of functionalised siloxanes with alumatrane: Reaction mechanisms and kinetics

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Abstract

Cross-linking of functionalised polysiloxanes is an important tool to adjust their viscoelastic properties and can be achieved by the reaction with alumatrane. The cross-linking reaction has been found to proceed only with hydrolyzed alumatrane species. Siloxane model compounds with different functional groups such as alkoxy, siloxy, and hydroxy groups were considered in order to optimise the rheological properties of the polymer. The activation energy barriers of the related reactions were analysed using the density functional theory under the assumption of the presence of Al–OH groups formed by the hydrolysis of alumatrane. The cross-linking involving hydroxy groups of siloxane and hydrolyzed alumatrane has been found to have the lowest activation energy (–14 kJ/mol). As the reaction of the Si–O–Si-polymer backbone with the hydroxy groups of the hydrolyzed alumatrane turned out to have the very low activation energy of +2 kJ/mol, this type of reaction is predicted to play a key role for the cross-linking of polysiloxanes with hydrolyzed alumatrane. The involved water molecules are formed back in the course of subsequent polycondensation reactions, therefore H₂O can be considered as a cross-linking catalyst in these systems.

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1. Introduction

Polymer-derived ceramics are presently considered to exhibit unusual thermomechanical stability [1,2]. The particular properties are discussed to be related with the unique microstructure controlled by nanodomains [3]. The formation of poly(organosiloxane)-derived silicon oxycarbide-based ceramics and fibres is controlled by the details of the involved cross-linking mechanisms which determine the thermomechanical properties and the chemical stability of the produced materials. In general, functionalised siloxanes are widely used single-source precursors as their preformed Si–C and Si–O bonds ensure high homogeneity of the composition at the nanometre scale. While the presence of covalently bonded car-

bidic carbon improves significantly the mechanical properties and the thermal stability, the additional introduction of selected main-group elements, such as boron or aluminum, favours the thermomechanical properties of Si–O–C ceramics further [4,5]. The aluminium-containing Si–O–C compositions have been found to contain a smaller amount of carbon as compared with the Al-free SiOC, they resist crystallization up to 1500 °C in Ar and do not form cristobalite during high temperature annealing [4,6].

Siliconoxycarbides are considered to show thermodynamic metastability under the applied synthesis conditions and have low self diffusion coefficients due to the presence of predominantly covalent bonding. Thus, conventional solid-state reaction of e.g., silicon carbide with silica cannot be used for the preparation of homogeneous ternary and multinary oxycarbides. Mainly, “soft chemistry” methods such as sol–gel techniques have to be applied to synthesize the required complex compositions [7].

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Among different reactants for the preparation of Al-containing ceramics by means of sol–gel methods, alumatrane, which can easily be prepared from the hydroxide, is one of the most convenient ones [4]. It is less sensitive to hydrolysis, compared to other alkoxide homologues, and, therefore, can be more controllably hydrolyzed and co-condensated in the presence of suitable polymers avoiding phase segregation in the multi-component chemical systems [8,9].

Little is known, however, about the polycondensation reaction of hydrolyzed alumatrane with siloxanes, containing functional groups other than hydroxy groups. In contrast to conventional silicon-containing precursors, which are used for the preparation of silica-gel based polymers by means of polycondensation of hydroxy groups, commercial polysiloxanes contain quite a few hydroxy groups, so that the participation of other functional groups in the cross-linking may be rate determining. The possibility to cross-link polysiloxanes with alumatrane in non-dried isopropanol has been shown by Harshe et al. [4]. As the gelation does not proceed in dried non-aqueous solvent, the presence of water – even though only traces – is affordable for the reaction to proceed.

In the present paper, the reaction mechanisms of the polycondensation of alumatrane with polysiloxanes are investigated using both experimental and theoretical methods. In particular, insight is provided into details of the cross-linking and the factors influencing their kinetics, based on quantum mechanical calculations using the density functional theory (DFT).

2. Experimental

The polysiloxane used for this research was a product from Wacker Chemie GmbH, Burghausen, with a trade name Wacker–Bensil PMS MK (MK polymer). The MK polymer is a solid and solvent free poly(methylsilsesquioxane) with $(\text{CH}_3\text{-SiO}_{3/2})_x$ as the basic structural unit and falls under the silicone resin group. The odourless, colourless flakes of MK-polymer has a softening range between 45 and 60 °C and a good solubility in organic solvent; namely, aromatic solvents and ketones. The polymer possesses approximately 2 mol.% hydroxy and ethoxy groups as functional units. Accordingly, the possible structure of the resin used along with its functional groups is illustrated in Figs. 1 and 2.

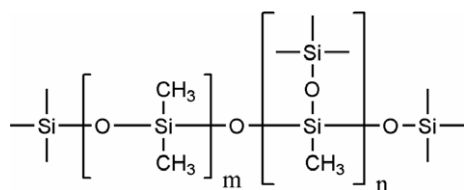


Fig. 1. Molecular structure of MK-polysiloxane with linear and branched components.

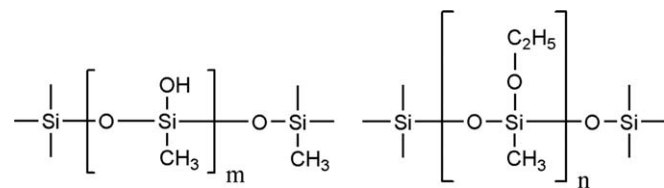


Fig. 2. Hydroxy and ethoxy groups as functional groups present in MK-polysiloxane.

Alumatrane (commercial Al-alkoxide from ABCR) with the general composition: $\text{C}_6\text{H}_{12}\text{NO}_3\text{Al}$ was used as an aluminum modifier. The yellowish coloured powder with a density of 1.05 g/cm³ is sensitive to moisture and must be stored in a dry place. Alumatrane was dissolved in isopropanol in different mass ratios, namely 2.5, 9.1, 16.6, and 23.6 wt.% followed by dissolution of the polysiloxane MK in isopropanol. Dissolution of both components was done in an ultrasonic mixture at room temperature. A polysiloxane:isopropanol ratio of 4 g:25 mL was kept constant for all the mixtures. A sol–gel transition takes place at room temperature forming a yellowish milky white residue. A very low amount of alumatrane, namely 2.5 wt.% does not transform to a gel state at room temperature and instead requires temperature of 50 °C for 5 h. All gels were dried at 85 °C in air for 24 h, ball milled and finally sieved to particle size <63 μm.

3. Computational details

The DFT approach, as implemented in GAUSSIAN 03 program, has been used (i) to find stationary points on the potential energy surface (PES) (ii) to optimize corresponding geometries, and (iii) to perform single-point energy calculations. For the geometry optimizations, the B3LYP hybrid exchange–correlation functional has been used along with the 6-31G(d) Gaussian-type basis set and the Berny optimization algorithm. The transition states have been localized by searching for the stationary points of first-order on the PES, while calculating the Hessian analytically at each optimization step. The internal reaction coordinate (IRC) path has been followed along the lowest (negative) frequency mode, starting from the transition state found (saddle point of the first order) down to the next local minima to ensure the relevance of the initial and final complex geometries to the transition state. For the single-point energy calculations the BH&HLYP hybrid exchange–correlation functional has been used, along with 6-311+G(3df,2p) basis set.

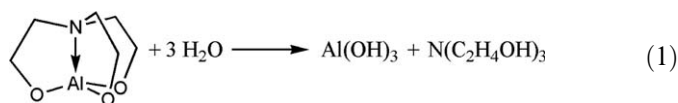
4. Results and discussion

4.1. Synthesis of cross-linked aluminum-containing polysiloxanes

Modification of poly(methylsilsesquioxane), MK polymer, with aluminum was studied by two routes, namely

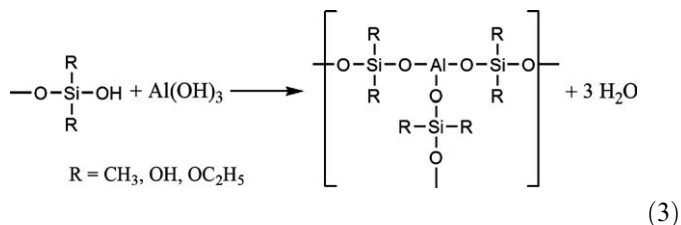
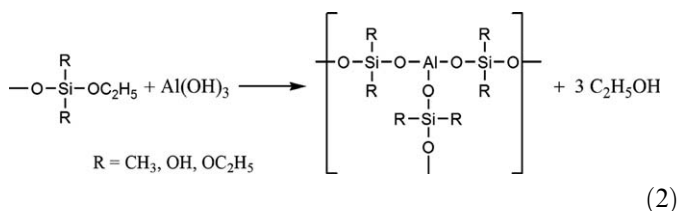
by the dissolution of solid alumatrane in molten polysiloxane without any solvent (melting route) and by dissolving the two reactants in a suitable solvent (solution route). In the melting route the alumatrane was added to the MK polymer and the mixture was heated to various temperatures (80, 100, 120, 140 °C). These temperatures were used as the polymer has a softening temperature at 60 °C. It was found that, at all temperatures, alumatrane cannot be dissolved in the polysiloxane and two liquid phases with alumatrane at the top were formed. No marked changes in the viscosity are observed, even if the melts are isothermally held for a long time at the above mentioned temperatures. After solidification by cooling to room temperature and reheating the mass again shows the same melting behaviour. This finding indicates that it is not possible to modify the MK polymer by aluminum alkoxide by melting, as the polymer is not cross-linked.

In the solution route, the polysiloxane and alumatrane were dissolved in a solvent between room temperature and 50 °C. The MK polysiloxane contains hydroxy, ethoxy and methoxy groups as functional groups, which can react with metal alkoxides resulting in cross-linking via polycondensation. Cross-linking reaction of MK polymer with aluminum alkoxide compounds like alumatrane used in this work proceeds via a sol–gel process at room temperature. The sol–gel transition is found here with isopropanol as a solvent. Sols prepared in acetone, methanol, ethanol, diethyl ether or *n*-hexane do not transform to gel at room temperature. Alumatrane reacts to a gel-like state with MK polymer in the presence of non-dried isopropanol by alcoholysis or hydrolysis and subsequent polycondensation. According to our experimental studies and taking into account that solvent free alumatrane and MK polysiloxane did not show any reaction, we assume that in a first step alumatrane is hydrolyzed by the residual water of the isopropanol used. Hydrolysis of alumatrane results in the formation of aluminum hydroxide as represented by reaction Eq. (1).



The formation of $\text{Al}(\text{OH})_3$ is also confirmed by the presence of triethanolamine $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ which could be analysed by in situ mass spectroscopy of the as synthesized gel during thermal analysis [6].

In a second step, aluminum hydroxide $[\text{Al}(\text{OH})_3]$ reacts with MK polysiloxane by a condensation reaction under release of ethanol and water as shown in reaction Eqs. (2) and (3).



Increasing the alumatrane content changes the colour of the polymeric gel from white to faint yellow. The gel time is dependent on the amount of alkoxide present. Gel time of 2, 5, and 11 h was observed for the 9.1 (SiAlOC1), 16.6 (SiAlOC2) and 23.6 wt.% (SiAlOC3) alumatrane mixture, respectively. A very low amount of alumatrane, namely 2.5 wt.% does not transform to a gel state at room temperature and instead requires temperature of 50 °C for 5 h.

4.2. Reaction mechanisms and activation energy barriers

Alumatrane, as many other aluminum molecular compounds, tends towards oligomerisation and is known to form predominantly dimers in the solution [10]. Due to the relatively good shielding of the Al atom with the trialkoxamine group and the relatively strong donor–acceptor bonding between aluminum and amine nitrogen, the alumatrane itself does not react with polysiloxanes as also proved experimentally. At least small amounts of water are needed to start the polycondensation reaction with

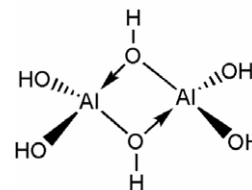


Fig. 3. The $\text{Al}_2(\text{OH})_6$ model cluster, representing the hydrolyzed alumatrane.

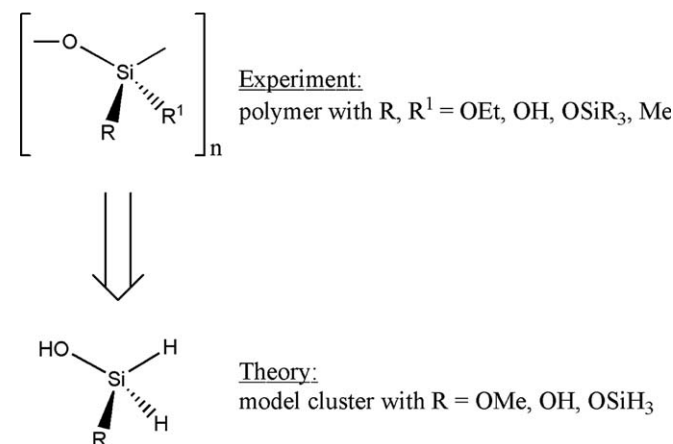


Fig. 4. Derivation of the $(\text{HO})_2\text{SiR}$ model cluster for the silicon-containing reactant.

polysiloxanes, so that the actual reaction proceeds between hydrolyzed alumatrane and polysiloxane. Based on these considerations, we used a hydrolyzed alumatrane as a model reactant, to investigate the substitution of hydroxy groups on Al with different functional groups of siloxanes.

The hydrolyzed alumatrane has been approximated by an $\text{Al}_2(\text{OH})_6$ cluster in the calculations (Fig. 3). Choosing this model, we took into account the usual tetrahedral coordination of aluminum in solution-derived, partially condensed aluminum hydroxides. Although such a cluster, once formed in a real experiment, would not be stable as a finite cluster for a longer time, it is nevertheless applicable as a theoretical model, as it reproduces the local chemical properties of the aluminum atom and the hydroxide group, also in higher condensed aluminum hydroxides with tetrahedrally coordinated aluminum. The tetrahedral coordina-

tion of aluminum provides a possibility for the coordination of nucleophilic species at the aluminum atom in the nucleophilic substitution reaction, according to an $\text{S}_{\text{N}}2$ mechanism.

To represent different functional groups at the silicon atom in polysiloxanes, a $(\text{HO})\text{H}_2\text{SiR}$ model cluster was used (Fig. 4), which enables to study the local properties of the functional group R in the gelation reaction with the aluminum-containing reactant. This model allows the evaluation of the reactivity of different functional groups in siloxanes, as the residual substituents at the silicon are expected to cause at the most a parallel shift of the potential energy surface near the reaction path.

Three different substituents – $\text{R} = \text{OH}$, OCH_3 and OSiH_3 – have been considered in the model reactions (Fig. 5). The substituent – OSiH_3 – represents non-specific

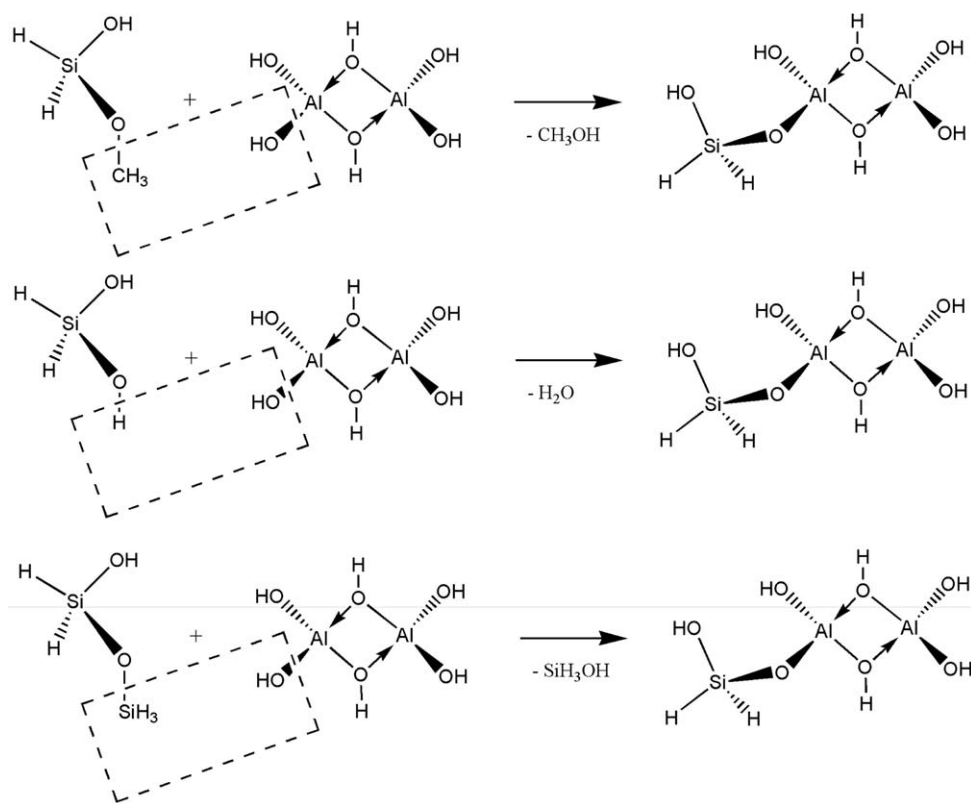


Fig. 5. Model reactions between $(\text{HO})\text{H}_2\text{SiR}$ and $\text{Al}_2(\text{OH})_6$ considered in DFT calculations.

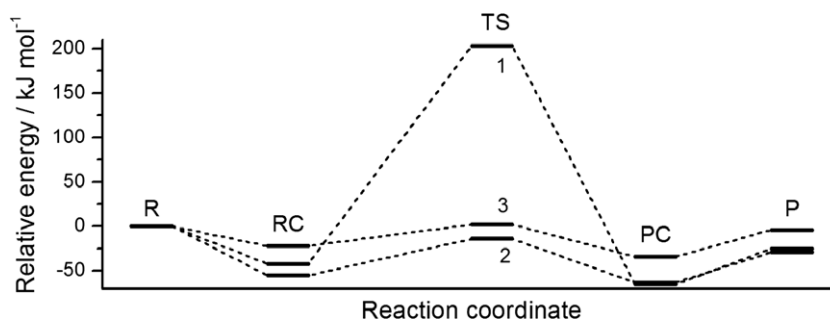


Fig. 6. Relative energies of reactants, products and intermediate complexes along the reaction path for the reactions in Fig. 5 (R, separate reactant molecules; RC, reactant complex; TS, transition state; PC, product complex; P, separate product molecules).

siloxo groups in general, so that the related model reaction also allows describing the relative reactivity of the Si–O–Si backbone with the hydrolyzed aluminum alkoxides. The two other model groups approximate the common substituents in polysiloxanes such as the hydroxy and alkoxy groups.

As the cross-linking of the Si–OR and HO–Al fragments proceeds according to a S_N2 nucleophilic substitution mechanism, the silicon-bonded oxygen participates firstly in the five-fold coordination of the aluminum in the transition state geometry. Then the R group is transferred to the OH group at the aluminum atom, which is accompanied with a charge separation that determines the height of the activation energy barrier for the reaction.

The results of the DFT calculations demonstrate that the reactivity of the siloxanes in the condensation reaction with hydrolyzed alumatrane varies strongly depending on the stability of the R^+ cation (where $R = CH_3, H, SiH_3$), which is formed during the transfer of R from the silicon bonded to the aluminum bonded oxygen, due to the charge separation. The highest activation energy barrier is found for $R = CH_3$. The condensation reaction of siloxane involving –OH and –OSiH₃ substituents with hydrolyzed alumatrane is characterised by relatively low activation energy barriers (–14 and +2 kJ/mol, resp.; cf. Fig. 6 and Table 1), indicating a high reactivity of the Si–O–Si backbone of polysiloxane with hydrolyzed alumatrane, thus, a rearrangement of bonds in the polysiloxane may occur. This provides an effective way of cross-linking polysiloxanes, even if the residual groups of the silicon are not able

to participate in a polycondensation process. According to the suggested scheme (Fig. 7), during the reaction of the Si–O–Si backbone with hydrolyzed alumatrane the hydroxy group is transferred from the aluminum to the leaving silicon atom, and an Al–O–Si fragment forms. The resulting hydroxy group at the silicon atom will react subsequently with the hydrolyzed aluminum alkoxide or can participate in the polycondensation process with other hydroxy groups in the siloxane.

It should be pointed out that only small (catalytic) amounts of water are necessary to initiate the cross-linking of alumatrane with siloxanes, which are available as soon as water is formed back in the result of the polycondensation. This explains the experimentally observed fact that the reaction with alumatrane proceeds already in the presence of water traces, but does not take place in absolutely dry solvent.

5. Conclusions

Aluminum-containing polysiloxanes were prepared by the reaction of alumatrane with a commercially available polysiloxane in isopropanol as the solvent. The polycondensation reaction proceeds in the presence of small amounts of water, resulting in the formation of cross-linked polysiloxanes. In the absence of solvent, however, no polycondensation reaction has been detected during melting the initial mixture of polysiloxane with alumatrane. This can be explained by the fact that the aluminum atom as an electrophilic centre is shielded by surrounding groups, and thus it is not available for the nucleophilic substitution reaction in the alumatrane molecules themselves.

The theoretical studies of the cross-linking reaction between hydrolyzed alumatrane and siloxanes containing different functional groups were performed in the frame of cluster approximation. They indicate that an alternative cross-linking process plays a key role in those cases where not enough hydroxy groups are available in siloxane for the commonly expected polycondensation to proceed. The Si–O–Si backbone of the polysiloxane can participate in

Table 1
Relative energies of reactants, products and intermediate complexes along the reaction path for the reactions in Fig. 5 (kJ/mol)

| | Reactant complex | Transition state | Product complex | Separate products |
|-----------------------|------------------|------------------|-----------------|-------------------|
| R = OCH ₃ | –42 | +203 | –65 | –25 |
| R = OH | –55 | –14 | –63 | –29 |
| R = OSiH ₃ | –22 | +2 | –34 | –4 |

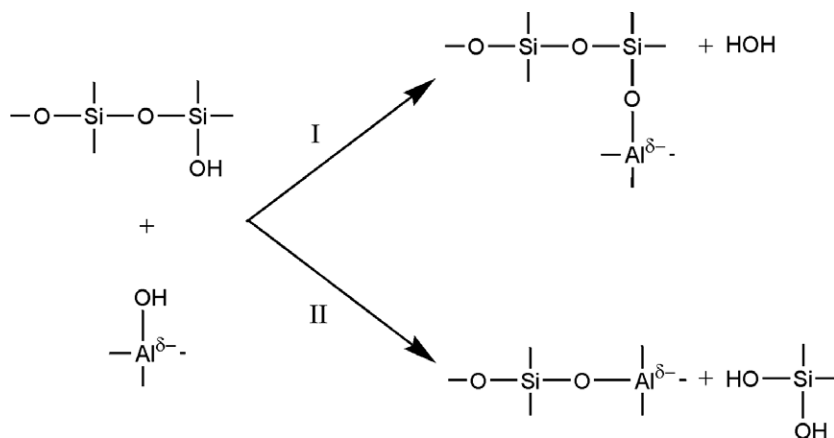


Fig. 7. Proposed paths of the cross-linking of siloxanes with hydrolyzed alumatrane.

the reaction with the hydrolyzed alumatrane species to form Al–O–Si fragments, thus enabling the cross-linking of polysiloxanes even in the absence of suitable reactive groups (like –OH) at the silicon atoms. This alternative polycondensation mechanism is characterised by a calculated activation energy barrier in a model reaction of +2 kJ/mol, which is very low in comparison with that of the reaction involving alkoxy groups on silicon (+203 kJ/mol). Only catalytic amounts of water are needed for the cross-linking between siloxanes and hydrolyzed alumatrane to proceed, as water is formed back in the course of this process.

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