

THE REACTIVITY OF TiO₂ AND ZrO₂ IN ORGANICALLY MODIFIED SILICATES

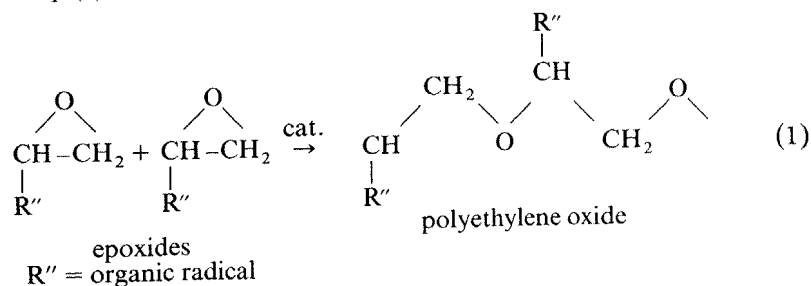
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The objective of this investigation was to compare the influence of titania, zirconia and silica on synthesis and properties of epoxide group containing organically modified silicates. These materials were prepared from the epoxysilane (MeO)₃SiC₃H₆OCH₂CHCH₂O and titanium, zirconium and silicon alkoxides by the sol-gel process. The results show that titanium and zirconium, beside their role as network formers, act as efficient catalysts for epoxide polymerization. Zirconium promotes thermally the polymerization of epoxides to polyethylene oxide crosslinking chains, whereas titanium promotes this reaction photochemically. The incorporation of crosslinking polyethylene oxide decreases the scratch resistance of the silicate condensates. The activity of silicon in both reactions is very poor.

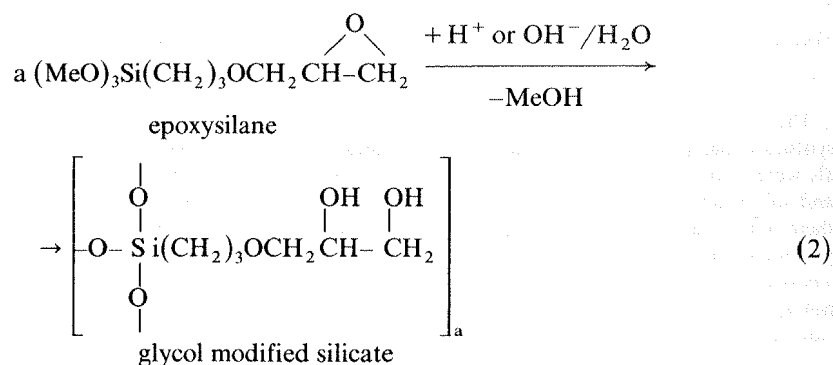
1. Introduction

The preparation of organically modified silicates as a first step involves the hydrolysis and condensation of silicoesters and related compounds and organically substituted silicoesters as precursors. Two basically different types of organically modified silicates have been developed. The first type is characterized by an inorganic network containing organic network modifiers of the type R'_nSiO_{(4-n)/2} (n = 0-3). The second type is characterized by an inorganic network, too, and in addition to this, by an organic network which is covalently bound to the inorganic one [1,2]. Different polymerizable radicals R' may be used for this purpose. In organic chemistry e.g. polymers of epoxides play an important role. A rough scheme of epoxide polymerization is given in eq. (1).



It has been shown elsewhere [3] that with an epoxy group containing silanes in connection with other network formers like TiO₂ and ZrO₂ monolithic and

coating materials can be prepared by the sol-gel process, but no mechanical investigations have been carried out so far. The sol-gel process generally includes the use of catalysts like acids or bases. It is well-known that under acid conditions epoxides may be reacted with water to form glycols as shown for an epoxysilane by eq. (2) [4]. That means hydrolysis and condensation have to be carried out very carefully, if water addition to the epoxides is to be prevented.



In order to perform the epoxide polymerization catalysts have to be used. It is known that $Ti(OR)_4$ and $Zr(OR)_4$ may act as catalysts for this reaction [5-11], whereas similar properties are not known from $Si(OR)_4$. Therefore, it is of interest to find out in which way these alkoxides act as catalysts in connection with the epoxysilane $(\text{MeO})_3\text{SiC}_3\text{H}_6\text{OCH}_2\text{CHCH}_2\text{O}$ while building up the inorganic hetero network. The main objective of this paper is to investigate mechanical questions during polycondensation and polymerization.

2. Experimental

In order to perform the condensation reaction $Si(OR)_4$, $Ti(OR)_4$ or $Zr(OR)_4$ were mixed with the epoxysilane in the 1:1 molar ratio. 1 mol. of such a mixture was stirred for 2 h with 10 g of silica gel. The silica gel had been loaded with 1/16 of the amount of water which is necessary for the complete hydrolysis of the alkoxy groups (stoichiometric amount). After this the silica gel was removed by filtration. Another 2/16 of the stoichiometric amount of water was added to the filtrate. The low viscous products were defined as precondensates and stored in a moisture-free atmosphere. In order to complete the hydrolysis the stoichiometric amount of water containing 0.1 mol. HCl/l was added. These mixtures were stirred at room temperature for another 2 h and heated afterwards to 70°C for 30 min. In order to prepare monolithic products the volatile components water and alcohol were removed by vacuum treatment. The remaining highly viscous fluids could be poured into moulds and cured at temperatures up to about 150°C to hard monoliths. The viscosities of the precondensates were determined by a capillary viscosimeter. Thereby

the precondensates were used undilutedly. For the determination of epoxy groups the precondensates were reacted with a mixture of $\text{Et}_4\text{NBr}/\text{HClO}_4$. The consumption of hydrobromic acid was determined by a potentiometric titration [12]. NIR spectra were measured from films between glass slides. The scratch resistance of solids was determined by scratching with a Vickers diamond loaded by different weights.

3. Results

3.1. Partial condensation and polymerization

The addition of water to $\text{Ti}(\text{OR})_4$ or $\text{Zr}(\text{OR})_4$ containing systems leads to the precipitation of TiO_2 or ZrO_2 . In order to avoid precipitation it is necessary to add water very carefully. For that purpose it was found out that it is very convenient to introduce the suitable amount of water by use of water loaded silica gel. No complication was expected from the immediate addition of water to the $\text{Si}(\text{OR})_4$ containing system. But for reasons of comparison the silica gel method was applied to all three systems. After the addition of 3/16 of the stoichiometric amount of water the viscosities of the resulting precondensates were determined by capillary viscosimetry as a function of time. Fig. 1 shows the results. In order to find out whether the increase of viscosity is due to the inorganic crosslinking or to the epoxide polymerization the remaining epoxy groups were analyzed after about 400 h reaction time. The results are given in fig. 1, too, where the data relate to the origin of epoxide contents. There is a reasonable correlation between the viscosity and the consumption of epoxides. Additionally in the NIR spectra where glycols show an absorption band at about 2050 nm no glycol groups could be detected. So it is supposed that the increase of viscosity of $\text{Zr}(\text{OR})_4$ and $\text{Ti}(\text{OR})_4$ containing precondensates is due

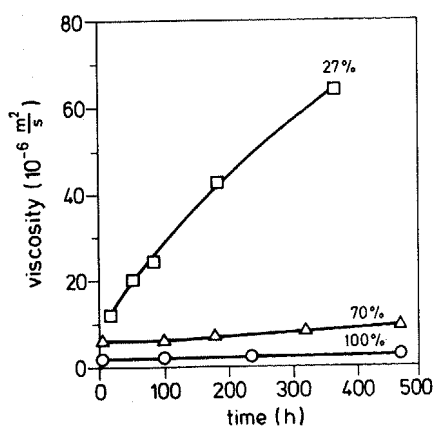


Fig. 1. Viscosity behaviour of precondensates from (in mol.%): ○ 50 epoxysilane/50 $\text{Si}(\text{OMe})_4$; △ 50 epoxysilane/30 $\text{Si}(\text{OMe})_4$ /20 $\text{Ti}(\text{OEt})_4$; □ 50 epoxysilane/30 $\text{Si}(\text{OMe})_4$ /20 $\text{Zr}(\text{OPr})_4$. Numbers in % indicate the remaining epoxides related to the origin amount. Storage at room temperature only.

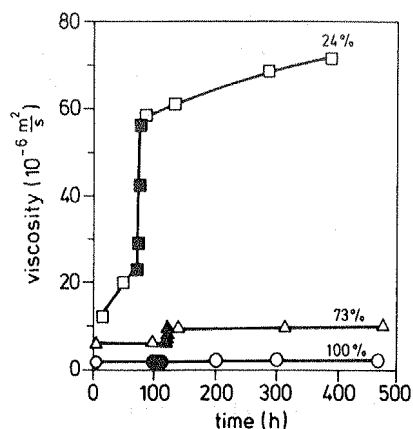


Fig. 1. Heat treatment at 70°C for 8 h (period indicated by full symbols \bullet , \blacktriangle , \blacksquare). Residual periods: storage at room temperature. For further details see fig. 1.

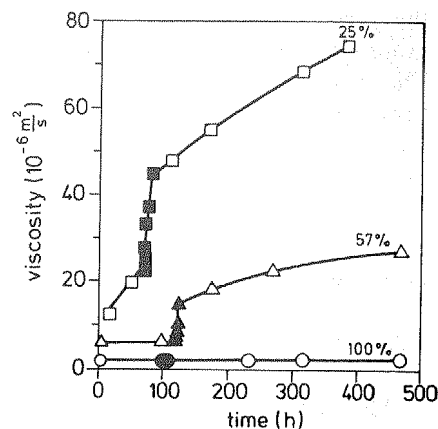


Fig. 3. UV-irradiation at 60°C for 8 h (period indicated by full symbols \bullet , \blacktriangle , \blacksquare). Residual periods: storage at room temperature. For further details see fig. 1.

to the partial epoxide polymerization according to eq. (1). The $\text{Si}(\text{OR})_4$ containing system does not show any remarkable reaction as expected.

During the next series of experiments the influence of temperature was investigated. Therefore the precondensates were heated for 8 h at 70°C and their viscosities were measured as a function of time. The results are shown in fig. 2. The increase of viscosity of the heat treated $\text{Zr}(\text{OR})_4$ containing precondensate is remarkably higher than that of the precondensate stored at room temperature for the same time. The behaviour of the heat treated $\text{Ti}(\text{OR})_4$ containing system is not very different from that only stored at room temperature and the $\text{Si}(\text{OR})_4$ containing system does not show any remarkable reaction at all. The results of the analysis of the epoxy groups are given in fig. 2, too. In the case of the $\text{Zr}(\text{OR})_4$ containing system the remaining amount of 24% of the original epoxides seems to be something like a limit under the applied reaction conditions. The reactivity of $\text{Ti}(\text{OR})_4$ to epoxides is hardly influenced by the applied thermal conditions which is unusual.

Since titanium (IV) is able to perform photocatalysis in a series of experiments the precondensates were irradiated by UV-light, too. The temperature of this reaction was about 60°C . The viscosities of these precondensates as a function of time are shown in fig. 3. The $\text{Zr}(\text{OR})_4$ containing system now reacts slower than at 70°C , that means it seems not to be influenced by UV-light. The $\text{Ti}(\text{OR})_4$ containing system, however, reacts far quicker than without UV-light whereas the $\text{Si}(\text{OR})_4$ containing system again does not react. The results of analysis of the epoxy groups are given in fig. 3, too. One can conclude from these experiments that in the $\text{Ti}(\text{OR})_4$ containing system a photocatalytic mechanism leads to a partial epoxide polymerization according

to eq. (1). The NIR spectra showed that neither in the $\text{Zr}(\text{OR})_4$ nor in the $\text{Ti}(\text{OR})_4$ containing system were glycol groups formed.

In order to find out whether the unhydrolyzed metal alkoxides or their precondensates are catalytically active, experiments were carried out to determine the increase of viscosities of the unhydrolyzed mixtures of $\text{Ti}(\text{OR})_4$ or $\text{Zr}(\text{OR})_4$ with the epoxysilane. In opposition to the precondensates these mixtures formed white precipitations at room temperature or solidified to opaque smeary materials during temperature and UV treatments. Therefore the determinations of viscosity and of epoxide content failed. The polymer types formed under this water-free conditions could not be identified.

3.2. Further treatments

In order to continue the inorganic crosslinking by hydrolysis and condensation HCl containing water was added to the precondensates. In the case of the $\text{Zr}(\text{OR})_4$ and $\text{Ti}(\text{OR})_4$ containing systems highly viscous products were received. The $\text{Zr}(\text{OR})_4$ containing system yielded remarkably higher viscosities at similar dilutions. In the case of the $\text{Si}(\text{OR})_4$ containing system only a slow increase of viscosities was observed.

Solid materials could be prepared from these hydrolyzation products by pouring the viscous fluids into moulds and curing them by heat treatment up to 150°C . With TiO_2 and ZrO_2 monoliths could be achieved (rods 10 cm in length and 2 cm in diameter). The SiO_2 containing system did not yield monolithic products. The curing process leads to cracks and to disaggregation of the materials into granulates. It is not quite clear whether this effect is due to the high hydrolysis and condensation effectiveness of TiO_2 and ZrO_2 compared to SiO_2 or due to their higher effectiveness in epoxide polymerization.

In order to have some information about the mechanical properties of the solid products their surface hardnesses were determined by a scratch test. The results are given in table 1. It is shown that the TiO_2 containing system results

Table 1
Scratch resistance of condensates ^{a)} of the composition (in mol.%) 50 epoxysilane/30 $\text{Si}(\text{OMe})_4$ /20 $\text{M}(\text{OR})_4$ in dependence on precondensate treatment ^{b)}

Precondensate treatment	Scratch resistance ^{c)} in g in dependence on $\text{M}(\text{OR})_4$	
	M = Ti	M = Zr
Room temperature storage	150	30
Heat treatment	180	10
Irradiation treatment	170	10

^{a)} Cured at 100°C for 2h.

^{b)} Details see agenda figs. 1-3.

^{c)} Numbers indicate diamond load in g which does just not affect scratches.

in the best scratch resistance. The SiO_2 containing particles were very brittle and so it was not possible to obtain a reasonable scratch result.

4. Conclusions

It was shown that $Ti(OR)_4$ and $Zr(OR)_4$ in combination with the epoxysilane $(MeO)_3SiC_3H_6OCH_2\overline{CHCH_2O}$ as precursors act in two different ways: as network formers to build up an inorganic network and as polymerization catalysts for the epoxides. It was surprising that a room temperature and at higher temperatures the zirconium showed by far the highest activity. In opposition to this, the scratch test gave remarkably better results with titanium. Higher temperature treatments in the case of zirconium leads to lower scratch resistance, whereas in the case of titanium the opposite effect can be observed. If the scratch test is considered as a measure for the network density or for the degree of inorganic crosslinking, titanium can be considered as the better promoter for the inorganic condensation, zirconium as the better one for epoxide polymerization. As expected, titanium showed a photocatalytic effect. That means that titanium containing system offers the possibility of photocuring without additional catalysts.

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