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NEW MATERIALS FOR CONTACT LENSES PREPARED FROM Si- AND Ti-ALKOXIDES BY THE SOL–GEL PROCESS

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Methods of synthesizing materials for hard contact lenses were developed by hydrolysis and condensation of an epoxide substituted alkoxysilane and Ti-alkoxides. To enforce sufficient tensile strength, polymethacrylates were incorporated as linear crosslinking elements using a methacryloxy substituted alkoxysilane as a hook between the siliceous network and the polymer chain. The incorporation of titania led to dense monolithic products which could be cured only with some minor shrinkages. Good wettabilities [contact angles with water: $(25 \pm 5)°$] are due to glycol groupings formed by the epoxide radicals. O_2-permeabilities of $P = (13 \pm 1) \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1} result from the silicone-like $-O-\underset{|}{\overset{|}{Si}}-R$ structure elements, where R denotes a silicon–carbon bound organofunctional radical.

1. Introduction

Inorganic oxide glasses are usually produced by melting of glass forming compounds, and high temperatures have to be used in order to obtain homogeneous melts. The sol–gel process for glass preparation (by hydrolysis and condensation of e.g. alkoxysilanes and network modifiers) does not require such high temperatures, since the formation of the network by the condensation of reactive monomers usually occurs in the liquid phase at low temperatures [1]. Only temperatures in the range of T_g have to be applied to achieve densification to monolithic glasses.

Since these temperatures are in the range of 500–600°C, no organic compound incorporated into the network will survive this procedure, despite the latter seems desirable in some cases in order to modify the material properties. In principle, dense materials may be prepared at low temperatures by hydrolysis and condensation of organochloro- or organoalkoxysilanes, as shown by the manufacture of silicone.

The introduction of silicon–carbon bound organic radicals into a glass network offers a wide variability of the material properties. Thus, as was shown elsewhere [2–6], it is possible to combine "inorganic" and "organic" construction elements to develop materials with special properties by the sol–gel process. It should be mentioned that by organic modification it is possible to obtain monolithic and dense bulk materials at low temperatures. In this paper the development of materials for hard contact lenses by a special sol–gel route using organic modification will be demonstrated.

Table 1

Main property requirements for hard contact lens materials

Physical properties	density 1.1–1.2 g cm^{-3}, sufficient flexibility, high hardness, good scratch resistance,
Optical properties	refractive index $n_D^{20} > 1.43$, transmission > 98%,
Chemical properties	water absorbing capacity < 10 wt.%, low tendency of deposition of components of lachrymal fluid, chemical stability (no unlinked components of contact lens material; resistance to acids, bases, organic solvents, microorganisms, and UV-light),
Wettability	contact angle with water < 30° in the hydrated state,
O_2-permeability	permeability coefficient $P > 10 \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1}.

2. Problem and basic considerations

Materials for contact lenses require especially high O_2-permeabilities to maintain the O_2-supply of the cornea and good wettabilities to preserve the lachrymal film between the cornea and the contact lens (table 1). With respect to the O_2-permeability silicone rubber would be suitable, since its O_2-permeability ($P = 79 \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1}) is high enough to supply the cornea sufficiently [7]. (For lenses applied during day-time only, an O_2-permeability of $> 10 \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1} is required [8].) On the other hand, silicone rubber is very hydrophobic. Despite its extreme hydrophobicity (contact angle with water: 85–100°) it is used as a material for contact lenses [7]. This extraordinary O_2-permeability is caused by the dimethyl siloxane back bone $\dashv OSi(CH_3)_2 \dashv$. For the development of new materials for contact lenses it seems reasonable to take advantage of such

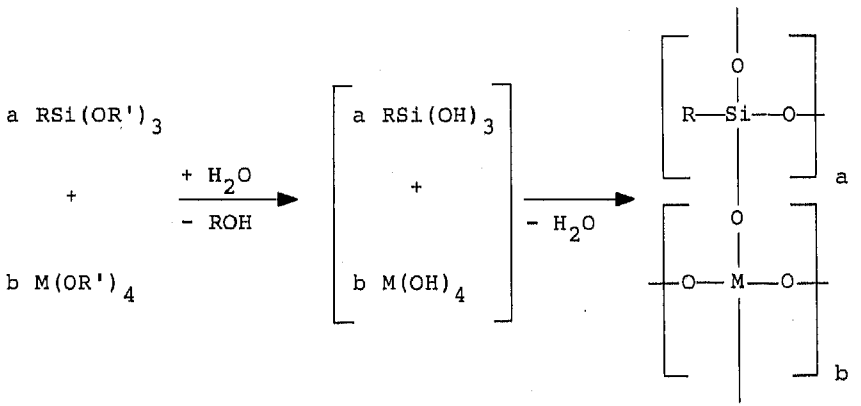

Fig. 1. Synthesis principle of an organically modified silicate. a = 1–100, b = 0–99 mol.%; R = hydrophilic radical, e.g. alkylen–OH; R' = alkyl; M = Si, Ti, Zr, etc.

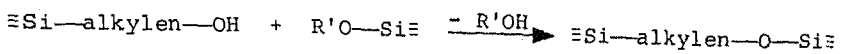

Fig. 2. Condensation possibility of silanes containing unprotected ≡COH groups.

groupings, e.g. $-O-\overset{|}{\underset{|}{Si}}-R$, but R should be a stable silicon–carbon bound hydrophilic organic radical.

To achieve wettability, alcoholic ≡COH groups have to be chosen, since ≡SiOH groups, as a consequence of its ionic character, adsorb proteins (components of the lachrymal fluid) rather well. The alcoholic groups should be attached to hydrolyzable and condensable silanes in order to be crosslinked to other components corresponding to fig. 1. But experiments showed that compounds of the type ≡Si–alkylen–OH under condensation conditions undergo the reaction corresponding to fig. 2, too. This leads to the disappearance of the important alkylen–OH groups and to the loss of wettability. Thus, it was necessary to use stable compounds with protected or latent ≡COH groups. This may be realized by the use of silanes containing epoxide groupings. Therefore the epoxysilane 1 (fig. 3) was checked with respect to its practical use. Herein, the alcoholic glycol group is latently included and only formed by the acid or base catalyzed addition of water corresponding to fig. 3 [9]. It was proved that under the same conditions the hydrolysis and condensation, caused by the $\equiv SiOCH_3$ groups, take place. This indicates that this reaction scheme may be used as a base for further steps.

3. Results

3.1. Synthesis and properties of condensates from epoxysilane 1 and silico-orthoesters $Si(OR')_4$ (R' = alkyl)

In principle, solid materials of type 2 (using only the epoxysilane 1 as the starting compound; see fig. 3) can be synthesized by this route. The derived products, however, were gel-like and disaggregated into small pieces during

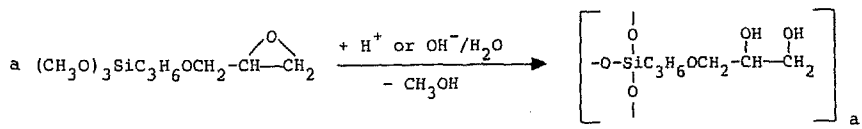

Fig. 3. Reaction of epoxysilane 1 with water (acid or base catalyzed).

curing; it was not possible to isolate any compact material within a practically reasonable curing time of some hours.

So it had to be ascertained , how denser materials with better mechanical properties could be synthesized. One way should be to increase the degree of polymerization by adding $Si(OR')_4$, since $Si(OR')_4$, contrary to $RSi(OR')_3$, leads to a fourfold binding. At the same time, the above-mentioned condensation procedure should be varied in order to avoid the undesired reaction of the once formed glycol groups to participate in the crosslinking corresponding to fig. 2. Therefore the following procedure was worked out: first, a nonhydrolytic condensation of the starting compounds, preserving the epoxide radical, was performed under reflux conditions with HCl as the catalyst corresponding to fig. 4 [9]. This reaction path was proved by GC/MS analysis of the reaction mixture, where R'Cl could be detected in considerable amounts; the latter corresponds to the results of ref. 10. Second, the hydrolysis of the epoxide radical under hydrolytic conditions was carried out.

Thus, the epoxysilane 1 and 5–30 mol.% $Si(OR')_4$ were refluxed first with alcoholic HCl. The products of this step were transparent fluids of low viscosities, still showing the characteristic bands of the epoxide radical in the IR spectra, but also a band of high intensity at 2870 cm^{-1} indicating unhydrolyzed alkoxides (≡SiOR'). That means that the starting compounds were only partially condensed. Then these precondensates were refluxed in aqueous HCl for hydrolysis and further condensation. This step was accompanied by a remarkable increase of viscosity. These liquid products were finally cured to transparent clear solids at temperatures above 100°C. The IR spectra of the solid products proved that there was no remarkable loss of glycol groups. But this procedure did not lead to crack-free products, although better mechanical properties were obtained than by use of the epoxysilane 1 only.

Therefore it was considered necessary to decrease the effect of shrinkages. One possibility was to enforce the condensation process by a suitable catalyst so that a higher degree of condensation could be reached during the liquid phase reaction, and, as a consequence, shrinkages during the curing could become less effective. From the literature Ti-alkoxides $Ti(OR')_4$ are known to be very efficient condensation catalysts [9]. Since these compounds act as network formers, too, it could be expected that no negative effect should be caused by them. For this reason, it seemed interesting to investigate, if $Si(OR')_4$ could be completely substituted by $Ti(OR')_4$.

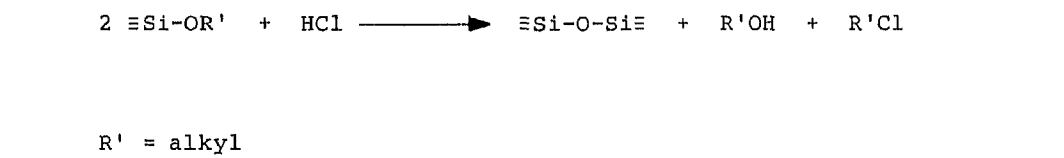

Fig. 4. Principle of nonhydrolytic condensation of alkoxysilanes.

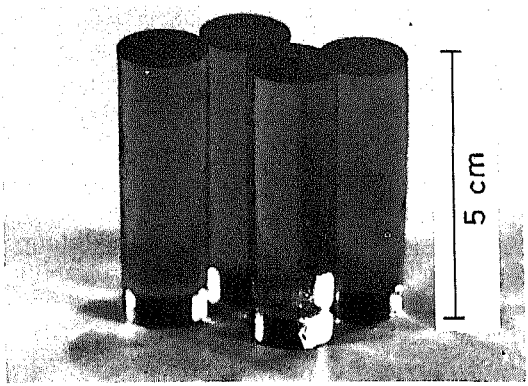

Fig. 5. Examples of monolithic condensates prepared from epoxysilane 1 and $Ti(OR')_4$.

3.2. *Synthesis and properties of condensates from epoxysilane 1 and titanium orthoesters $Ti(OR')_4$ (R' = alkyl)*

Contrary to $Si(OR')_4$, $Ti(OR')_4$ is hydrolyzed very easily in alcoholic solutions even with traces of water and forms TiO_2 precipitates. Therefore it was necessary to immobilize the $[TiO_4]^{4-}$ element in a prenetwork by the nonhydrolytic condensation process. By this means it was possible to crosslink $[TiO_4]^{4-}$ elements into the prenetwork so strongly that the subsequent hydrolytic step (complete hydrolysis of ≡TiOR', ≡SiOR', and the epoxide) did not lead to any precipitate at all.

Thus, mixtures of 1 and 5–20 mol.% $Ti(OR')_4$ were condensed by the described two-step procedure (see 3.1). In principle, the reaction path is comparable to that using $Si(OR')_4$ as proved by IR and NIR spectroscopy. The IR spectra of the precondensates still showed the characteristic bands of the epoxide radical at 3060, 1250, and 910 cm^{-1}. These bands no longer appeared in the IR spectra of the cured products, but the NIR spectra showed a band

Table 2

Main properties of solids prepared from epoxysilane 1 and 5–20 mol.% $Ti(OR')_4$, cured at 130°C

Contact angle with water [a] (°)	25 ± 5
O_2-permeability coefficient $P \times 10^{11}$ (ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1})	12.0 – 13.5
Refractive index n_D^{20} [b]	1.505 – 1.525
Density (g cm^{-3})	1.24 – 1.37
Mohs' hardness	3 – 4
Tensile strength [c] (MN m^{-2})	3.60 – 2.14
Modulus of elasticity $\times 10^{-2}$ (MN m^{-2})	34 – 29

[a] In the hydrated state.
[b] In the dehydrated state.
[c] Drafting speed 5 cm min^{-1}.

near 4880 cm^{-1} appointed to the glycol group. By adding aqueous HCl to the low viscosity precondensates, subsequent condensation occurred and liquids of high viscosities were formed which could be cured to solids at temperatures of 80–130°C without remarkable shrinkages. As a consequence, no cracking or disaggregation of the bulk occurred as shown in fig. 5.

The properties of these products are summarized in table 2. The good wettabilities of about 25° (almost independent of composition) have to be attributed to the glycol groups, since products containing methyl groups instead of glycol groups are very hydrophobic. The values of O_2-permeability are sufficient for contact lenses, but far from the O_2-permeability of silicone rubber. Obviously there is insufficient similarity to the silicone rubber structure. Whereas the refractive index, density and Mohs' hardness increase with increasing content of titania as expected, the inverse effect on the tensile strength is surprising. It can be explained by the increased brittleness caused by the higher degree of condensation due to the higher titania content.

These results show that the developed materials have the basic properties suitable for contact lenses. A comparison of wettability and O_2-permeability of commercial materials with that of the new materials shows their advantage (table 3).

In further investigation the ability to form lenses and their mechanical stability were tested. It was shown that these products could be conveniently formed by cutting and polishing, the usual manufacturing process of contact lenses. But contact lenses using these materials still fractured easily because of their poor flexibility and tensile strength. The reason for this may be the high degree of crosslinking of the network. Therefore it was considered necessary to incorporate linear crosslinking elements as a result of which the flexibility should be improved while the other good properties should be preserved.

Table 3

Comparison of wettabilities and O_2-permeabilities of materials for hard contact lenses [11]

Material	Contact angle [a] with water (°)	O_2-permeability coefficient $P \times 10^{-11}$ (ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1})
Epoxysilane 1/$Ti(OR')_4$ 95 : 5 mol.%	25	13.4
Menicon O_2 [b]	36	12.7
Perm-O_2 [b]	37	4.1
Alberta [b]	47	16.2
CAB	48	10.6
HCL-5 [b]	51	13.1
Supra O_2 [b]	51	13.1
Boston [b]	54	13.3

[a] In the hydrated state.
[b] Trade name.

3.3. Improvement of mechanical properties

Linear crosslinked polymers are mainly represented by silicone rubbers. They are well known for their good flexibilities. But with the exception of their extreme hydrophobicity, silicone rubbers show only poor mechanical properties. Therefore linear crosslinking elements had to comply with two requirements: first, they had to provide better mechanical properties than silicates or silicones, and second, they had to be crosslinked with the siliceous network by covalent bonding. Comparing the mechanical properties of known contact lens materials, it was found that polymethacrylates had much better tensile strengths than silicone rubber (e.g. polymethyl methacrylate (PMMA): 47–75 MN m^{-2}; silicone rubber: $\approx$ 10 MN m^{-2}) [7]. Moreover, there was a good possibility to crosslink methacrylates (as they are also used to improve the properties of silicones, by the way [12]) with the siliceous network, since a polymerizable and condensable component like the methacryloxysilane $(CH_3O)_3SiC_3H_6OOC C(CH_3)=CH_2$ was available. In principle, this component is able to act as a hook between the siliceous network and the methacrylate, respectively polymethacrylate as shown in fig. 6.

Thus, methacrylates were used as linear crosslinking elements. Methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were selected, since their polymers show some improved properties as contact lens materials: with PMMA no deposition of components of the lachrymal fluid is observed, and PHEMA is quite hydrophilic [7].

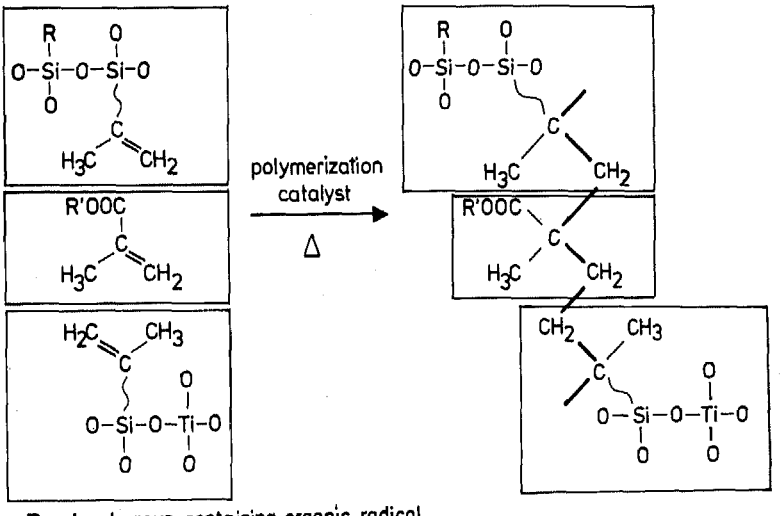

Fig. 6. Principle of crosslinking of the siliceous network using polymethacrylates.

Thus, a mixture of the epoxysilane 1, methacryloxysilane and $Ti(OR')_4$ in the ratio 90 : 5 : 5 mol.% was condensed by the two-step procedure (see 3.1) as long as the condensate could just be mixed homogeneously with 20–30 mol.% of monomeric methacrylate and with catalytic amounts of a peroxide polymerization catalyst. These highly viscous and still pourable mixtures were cured at temperatures up to 150°C, where the copolymerization and the further condensation of the siliceous network occurred. All products were formed without remarkable shrinkages, too; they were transparent, homogeneous, and dense solids like that shown in fig. 5.

Their properties are summarized in table 4. In this way, the tensile strength of the siliceous material could be improved by about 40%, whereas the modulus of elasticity remained almost unchanged. Consequently the mechanical properties, especially the flexibility, could be improved so much that contact lenses prepared from these new materials were flexible and could withstand handling and the applied tests. As expected, the hardness (see Mohs' hardness) and refractive index slightly decreased. Almost no change in wettability and O_2-permeability occurred. The better wettabilities of HEMA copolymers can be related to the higher ≡COH content and, as a consequence, to the higher water take-up (11–15 wt.% compared to 6–10 wt.% of MMA copolymers). Last, but not least, no deposition of the components of the lachrymal fluid was detected even on HEMA copolymers (after sevenfold treatment with synthetic lachrymal fluid); PHEMA hydrogels are especially known for their high tendency of deposition.

Thus, it was possible to improve the flexibility remarkably by the incorporation of linear crosslinking elements like polymethacrylates which have suitable mechanical properties and to preserve the other good properties like wettability and O_2-permeability.

Table 4

Main properties of copolymers [a] containing 20–30 mol.% methacrylates [b], cured at 130°C

Tensile strength [c] (MN m^{-2})	4.85 – 5.15
Modulus of elasticity $\times 10^{-2}$ (MN m^{-2})	33 – 34
Mohs' hardness	3
Shore *D* hardness	67 – 73
Refractive index n_D^{20} [d]	1.499 – 1.503
Contact angle with water [e] (°)	25 ± 5
O_2-permeability coefficient $P \times 10^{11}$ (ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1})	11.5 – 13.3

[a] Silicate composition: epoxysilane 1, 5 mol.% $Ti(OR')_4$ and 5 mol.% methacryloxysilane.
[b] Methacrylates $R'OOCC(CH_3)=CH_2$ with $R' = CH_3$, C_2H_4OH.
[c] Drafting speed 5 cm min^{-1}.
[d] In the dehydrated state.
[e] In the hydrated state.

5. Conclusion

Siliceous materials could be developed for hard contact lenses which display sufficient properties with respect to the above-mentioned requirements. The products consist of a siliceous network which is crosslinked by chains of polymethacrylates. The network was synthesized by the hydrolysis and condensation of an epoxysilane and Ti-alkoxides; in this way it was possible to unify the main requirements of good wettability and O_2-permeability in one and the same product. By the incorporation of polymethacrylates sufficient overall mechanical properties were obtained.

These investigations generally show the possibility of preparing monolithic siliceous materials with particular properties by the sol–gel route, if suitable inorganic and organic network formers and network modifiers are introduced.

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Discussion

The authors entered the old field of heteropolysiloxanes on a new route, the sol–gel route. It seems that a new impetus is given by the sol–gel process to the

direction of organically modified silicates, and not only for contact lenses, as other papers of this group have shown.

For instance, a question was asked about the possibility of the preparation of contact lens material for the controlled release of medicaments. The answer was that this question is in discussion but no work has yet been done.

C. Schüler asked for the chemical and mechanical stabilities of the new materials especially after ageing. *G. Philipp* answered that until now only the stability against the components of the lachrymal fluid has been investigated. The next steps will be to test the stability against acids, bases, organic solvents, microorganisms, and UV-light.

Questions by *F. Geotti-Bianchini* and *S.P. Mukherjee* regarding the method of production of the lenses were answered as follows. The examples mentioned were produced by a mechanized cutting process. Basically these materials allow the preparation of varying geometries directly without grinding and polishing. But because of the need for different individual shapes of lenses it may be more economic to produce them by individual machining.

Conclusion of Part 7

This session showed the combination of new basic chemistry and new chances of application.

Summarizing the chairman: the above-mentioned combination is just what is needed in the sol–gel field after more than ten years of development. The basic development must be continued but new products and new applications have to come, too. In this way, the basic research and product research will come closely together, thus broadening the sol–gel field. The interest of industry in this field is growing and we may hope that in the 3rd International Workshop "Glasses and Glass Ceramics from Gels" in Montpellier in 1985 some new sol–gel products will be presented.