

## NEW TYPE OF NON-CRYSTALLINE SOLIDS BETWEEN INORGANIC AND ORGANIC MATERIALS

H. SCHMIDT

*Fraunhofer-Institut für Silicatiforschung, Neunerplatz 2, D-8700 Würzburg, F.R.G.*

Increasing demands for special materials led to the conception of composites, since valuable properties of different types of materials can be combined. The question arises, whether combinations of different components are reasonable or possible on a molecular scale. General consideration of different principles of combinations are discussed and the sol-gel process as a useful tool in order to obtain glass related combination structures of inorganic and organic components is introduced. Some practical examples are given.

### 1. Introduction

If one starts to think about the combination of materials with very different properties, there is normally a very simple reason for combination: neither one nor the other of the single materials can satisfy the requirements for special applications. This consideration has led to various composite materials, like fiber reinforced plastics, laminates and others. One can say that the use of pure materials represents a minority, since in most cases at least one property of a pure material has to be corrected by a second one. Examples might be: coatings on metals (corrosion, design); glazes on ceramics (porosity, design); inorganic fibers in polymers (strength); fillers in polymers (strength, costs). In the past glasses were mainly used as typical non-composite materials. This is due to a couple of excellent properties of glasses like chemical durability, transparency and optical properties. But with increasing demands, like special optical and mechanical properties, glasses become more and more modified by other components, like special coatings (e.g. heat reflecting) or laminated by organic polymers (car windshields). This type of modification takes place on a macroscopic scale which means that a two or more step processing has to be applied. The increase of costs has to be equalized by the better properties of the composites.

The question arises, whether it makes sense to develop "composites on an atomic scale": if it is possible to develop new properties by this approach and if it is possible to synthesize such products on a large scale and in such a way that simple processing techniques may be used, there might be several advantages. At first the question has to be answered which possibilities exist to combine typical inorganic with organic structures. Therefore one has to consider the basic chemistry and physics of network forming processes. In the

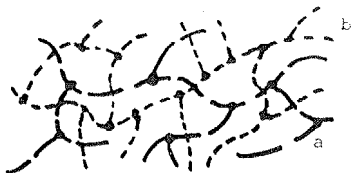


Fig. 1. Non-crosslinked networks of two types of polymers a --- and b ———; T  $\equiv$  crosslinking points within one and the same network.

case of the most common oxide glasses, the network forming grouping is the metal oxide (Me-O-Me) bond. For organic polymers different crosslinking groupings are common:  $\equiv\text{C}-\text{C}\equiv$ ,  $\equiv\text{C}-\text{O}-$ ,  $-\text{CO}-\text{N}=\text{}$ ,  $\equiv\text{C}-\text{N}=\text{}$  and others. Silicones normally use the  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  grouping, but  $-\text{O}-\text{Si}-\text{C}\equiv$  groupings in special cases are used, too [1]. This indicates a special case of an organic-inorganic crosslinking, if the silicone backbone is defined as an inorganic one.

In general, different theoretical possibilities for the combination of inorganic and organic networks are plausible: the simplest case would be random distributed chains or three-dimensional networks of both types without chemical bonds or other strong interactions in between (fig. 1). For this type of polymer the formation reaction of the both networks has to take place at the same time without leading to inhomogeneities like phase separation which can easily happen if the two networks are different e.g. in their hydrophilicity.

Better defined structures should be achievable by the introduction of crosslinking points between the two types of networks: these crosslinking points can be ionic, coordinative or covalent. In the ionic case mixed salt structures might be proposed (fig. 2). Coordinative crosslinking points are imaginable by the use of transition metal oxides with complex ligands like cyclopentadiene (fig. 3). The covalent crosslinking point has to use a stable covalent metal to carbon or metal to oxygen to carbon bond. In this case the  $\equiv\text{Si}-\text{C}\equiv$  bond has an exceptional position by reason of its high hydrolytic as well as (compared with organic compounds) thermal stability. The thermal stability of the  $\equiv\text{Si}-\text{O}-\text{C}\equiv$  grouping is at least as good as that of the  $\equiv\text{Si}-\text{C}\equiv$  grouping (tetraethoxysilane decomposes in dry atmosphere at  $T > 500^\circ\text{C}$  [2]), but its hydrolytic stability, with the exception of some special cases, is poor.  $\text{Me}-\text{C}\equiv$  or  $\text{Me}-\text{O}-\text{C}\equiv$  bonds of other elements in general are even

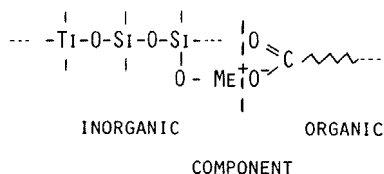
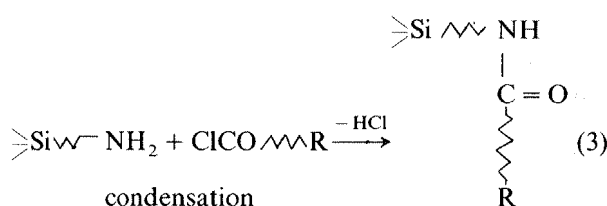
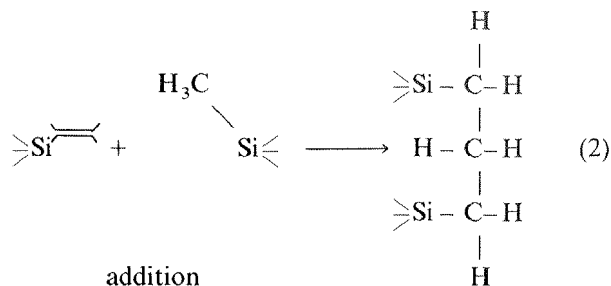


Fig. 2. Ionic crosslinking point between an inorganic and an organic network.





R e.g. - CH<sub>3</sub>

Eqs. (1)–(3) only demonstrate a few examples. Basically the wide variability of the organic chemistry might be applied. These reactions allow the introduction of an organic polymer network into a metal oxide polymer network, since in addition to eqs. (1)–(3) the copolymerization of pure organic monomers becomes possible and on the other hand, the variability of metal oxides from alkoxides, used by the sol–gel process, is pretty high, too.

Organic components do not necessarily have to act as network formers: if they are not polymerizable, they may act as network modifiers, since they decrease the degree of crosslinking by blocking bonds at the silicon atom (fig. 4). By these means, the properties of silicones are predetermined. Gullledge [13] and Adrianov et al. [14,15] could show that silicone type networks with inorganic heteroatoms are preparable. The effect of the decrease of crosslinking in those cases led to dense products without high temperature treatment. This demonstrates one clear advantage of this route: the incorporation of organics can make processing of bulk materials easier. In order to produce effects like these, the chemical nature of the organic grouping should not play that important role. But one can expect that the size of the grouping affects the structure strongly. Thus, differences should be expected e.g. from  $\equiv \text{Si}-\text{CH}_3$  or  $\equiv \text{Si}-\text{C}_6\text{H}_5$  groupings. It could be shown that the substitutions of  $-\text{CH}_3$  by  $-\text{C}_6\text{H}_5$  lead to very different properties of polymers [16,17]. Whereas  $-\text{C}_6\text{H}_5$  containing polymers are thermoplastic and soluble in most organic solvents, the corresponding  $-\text{CH}_3$  containing materials are insoluble and non-thermoplastic. This might partly be due to the lower degree of crosslinking in the case of phenyl groups as a result of a steric hindrance. In both cases dense materials could be synthesized which could be used as coatings.

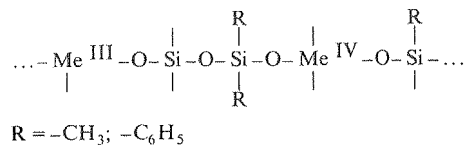


Fig. 4. Scheme of an inorganic polymer chain with R as network modifier.

Moreover, the use of organofunctional groups such as R (called "R'Y"; R e.g. alkylene) leads to the possibility to outfit an inorganic network with special organic functions. These might be acid or basic functions, special reactivities, wetting properties or ligands for the formation of complexes, e.g. transition metal complexes (fig. 5). If the described variabilities are summarized, an almost innumerable amount of possibilities is opened only by variation of composition. This will be extended by the variation of reaction conditions which may have a big influence on structure and on the material properties.

The question arises, whether materials based on these more general considerations might be regarded as glasses or not. They surely are not glasses in the classical sense, but they can be considered as an interesting modification of sol-gel derived materials.

## 2.2. Sol-gel variations

The preparation of sol-gel derived organic-modified materials (so-called organically modified silicates, since Si always has to be present) basically may follow the same rules as they are valid for the general sol-gel process, at least with respect to the first steps, hydrolysis and condensation. Differences may occur in the reactions rates as a function of the influence of the organic ligands (steric influences or change of electron density at the silicon atom). This may be of importance in multicomponent systems, since e.g. differences in hydrolysis rates result in differences of the concentration of reactive species and this influences crosslinking and structure strongly. How important these effects are is demonstrated by the hydrolysis reaction of  $(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$  ( $n = 0-3$ )

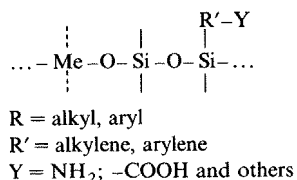


Fig. 5. Scheme of a "Y"-modified inorganic network.

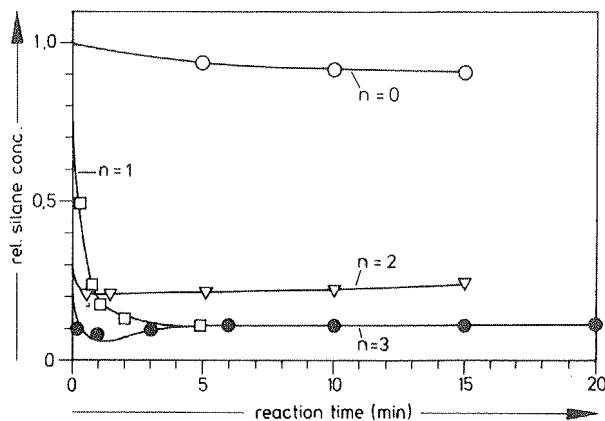


Fig. 6. Relative hydrolysis rate of  $(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$ ; volume ratio 1:1 in ethanol, with 0.002 mol. HCl/1 as catalyst.

(figs. 6 and 7). With HCl as the catalyst the methyl group containing species hydrolyse quicker than tetraethoxysilane. With  $\text{NH}_3$  the opposite behavior occurs [18]. It is rather difficult to give a satisfying mechanistical explanation. The effect might be due to the influence of the different ligands on the electron density of the silicon atom. Therefore special models for the transition state have to be adapted which are not proved in any case. But the effect of these differences in rates may be drastic: in the HCl catalyzed case, in the system  $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$  (I)/ $\text{Si}(\text{OC}_2\text{H}_5)_4$  (II), the hydrolysis of (I) is far faster than that of (II) (eqs. (4) and (5)).

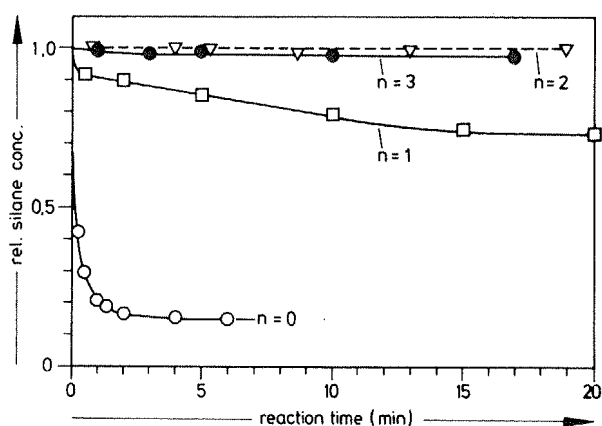
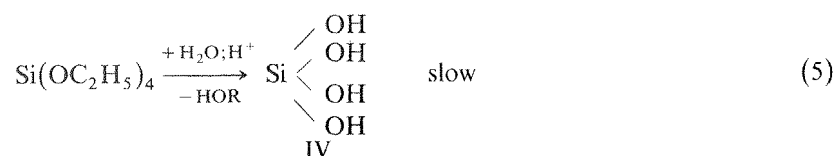
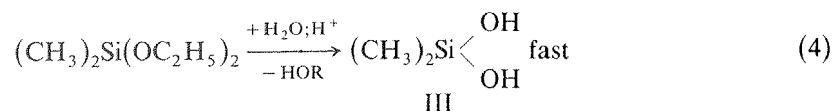


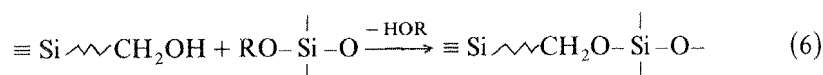
Fig. 7. Relative hydrolysis rate of  $(\text{CH}_3)_n\text{Si}(\text{OC}_2\text{H}_5)_{4-n}$  analogous to fig. 6, with 2 mol.  $\text{NH}_3$ /1 as catalyst.



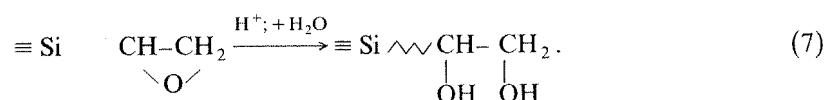
That means, a high concentration of III and a low concentration of IV are present at the beginning of the reaction which leads to polymerisates mainly consisting of III. With an advancing reaction the concentration of IV increases and will be incorporated into the polymers in increasing amounts. The use of  $\text{NH}_3$  as a catalyst just turns upside down.

This shows clearly how reaction conditions may influence structure. That means furthermore that it is of high importance to control the reaction rates of the different components and to evaluate the important parameters. The control of the reaction rate is of special interest, if components with extremely different rates have to be used or if side reactions may take place. Different hydrolysis rates may be expected from different substituents at the Si atom or from the use of different alkoxides, like the rapidly hydrolyzing  $\text{Ti}(\text{OR})_4$  and  $\text{Si}(\text{OR})_4$ . If the rate determined inhomogeneities should be avoided, it is necessary to control the addition of water. This opens the chance for partial hydrolyzed  $\equiv \text{TiOH}$  groups to react with  $\text{ROSi} \equiv$  groups in order to form  $\equiv \text{Ti}-\text{O}-\text{Si} \equiv$  bonds before totally hydrolyzed Ti species are able to form  $\text{TiO}_2$  precipitates [19,20].

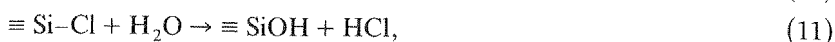
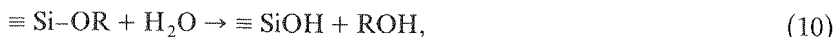
Side reactions can take place, if substituents are used which are able to act as condensable groups: for example, in order to receive hydrophilic materials (bulk or coating),  $-\text{CH}_2\text{OH}$  groups bound to the Si may be used. With such ligands a reesterification reaction can occur [21,22] (6),



and this would result in a loss of hydrophilic groups in the condensate. To avoid this, epoxides can be used and reacted to glycols by the addition of water, if it is possible to separate hydrolysis and condensation from the ring opening reaction (7) [20].



Since in general this reaction takes place under conditions where hydrolysis and condensation are carried out, the condensation has to be performed without water according to Voronkov et al. [2], eqs. (8)–(12).



Under these conditions it is possible to form condensates without the expoxide ring opening reaction taking place. During this process the formation of an oxide pre-network occurs and leads to a steric hindrance of the reesterification reaction during and after the glycol formation according to eq. (6), while further hydrolysis and condensation is performed.

The properties of the materials derived from organic-modified and non-modified alkoxides depend strongly on the type of monomers used as starting compounds. Generally speaking, the higher the amount of organic radicals, the softer the products appear, and, as a consequence, dense materials are preparable at very mild conditions (100–200°C). This is due to the decrease of the degree of crosslinking. Higher numbers of inorganic components lead to more brittle products and, under certain circumstances, to porous gels [22,23]. The proper selection of organic as well as inorganic functions may lead to the use of the gels as they are, e.g. as selective adsorbents, membranes or others. Densification of porous gels by heat in most cases results in the destruction of the organic functions. Better results may be expected by pressure densification.

### 3. Examples

#### 3.1. New contact lens materials

As mentioned above, it is possible to incorporate Si bonded alcoholic groupings into siliceous networks. If one compares the wetting angles of a  $\text{SiO}_2 : (\text{CH}_3)_2\text{SiO}$  (I) 30 : 70 molar ratio composition and a  $\text{SiO}_2 : \text{O}_{3/2}\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{CHOHCH}_2\text{OH}$  (II) 30 : 70 composition, one finds 90° for (I) and 20° for (II). It is remarkable that the low wetting angle appears despite (II) has a higher number of hydrocarbon units than (I). Wettability by alcoholic (non ionic) groups can be helpful for making contact lens polymers wettable. This is used by HEMA gels (hydroxyethyl methacrylate). The disadvantage of these gels is the high water content (30–70 wt%), since preservatives may be stored and microbes may contaminate the surface. Low water content (dense) organic polymers generally are hydrophobic and show a low  $\text{O}_2$  permeability which may lead to cornea diseases. With respect to the  $\text{O}_2$ -permeability dimethylsilicones are by far the best materials, but they are extremely hydrophobic. This leads to the idea of “wetable silicones” with alcoholic hydrophilizing groups, since the ionic SiOH groups show an undesired strong adsorption of proteins. Measurements on system II show sufficient



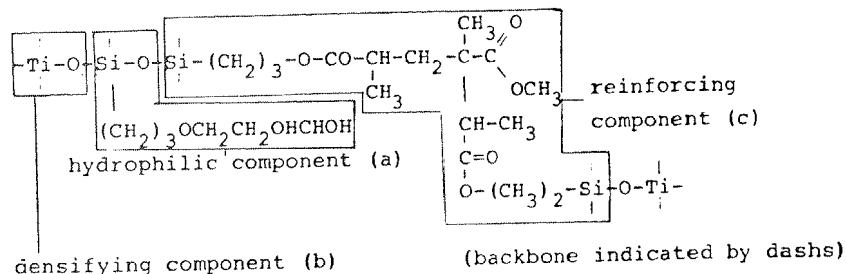


Fig. 8. "Construction principle" of a wettable,  $O_2$ -permeable hard contact lens material; molar ratio a:b:c = 65:5:30.

$O_2$  permeability, too ( $P = 12 \times 10^{-11} \text{ ml } O_2 \text{ cm}^2 \text{ ml}^{-1} \text{ S}^{-1} \text{ mm Hg}^{-1}$ ), but the mechanical properties of this gel-like material is very poor (brittle gel). The use of Ti alkoxides (Ti acts as a condensation catalyst) leads to dense materials with a reasonable modulus of elasticity and tensile strength. But only the reinforcement by organic polymerization in analogy to eq. (2) with methacrylates yielded in materials with practical useful properties (fig. 8) [19].

### 3.2. Scratch resistant coatings

Organic polymers are normally soft and sensible to abrasion and scratching. The question arises, whether the incorporation of inorganic components may increase the scratch resistance. The material in fig. 8 may also be considered as a reinforced PMMA. Pure PMMA has a very poor scratch resistance, the reinforced material according to fig. 8 shows a Mohs' hardness of about 4 which is very high for plastics. So the attempt was made to process a coatable prepolymer by an interrupted polycondensation reaction of  $(RO)_3\text{-Si}(\text{CH}_2)_3\text{OCH}_2\text{CHCH}_2\text{O}$ ,  $\text{Ti}(\text{OR})_4$  and  $\text{Si}(\text{OR})_4$ . Under stoichiometric addition of water with controlled  $\text{H}_2\text{O}$  releasing agents leads to products with predetermined viscosities which can be used as coating materials for organic polymers and other soft substrates and thus, scratch resistance can be proved substantially. The coating can be cured at  $100\text{--}120^\circ\text{C}$  within minutes [24].

### 3.3. Functional coatings

The modification of the covalent to silicon bond "Y" can be used for creating chemical by active surfaces, if it is possible to run the preparation in a such a way that Y appears at the surface. With  $\text{Y} = \text{NH}_2$  it could be easily proved that amino groups act as surface groups both with coatings and porous materials [24]. Amino groups can be used as coupling groups for biochemical materials like enzymes or antibodies [16] or as adsorption centers for acids [22]. But it is also possible to incorporate more complicated groupings for special purposes. With respect to the coupling of proteins (e.g. antibodies for radioimmunoassays) diazo groupings react to an irreversible covalent bond, with



The author wants to express his thanks to Professor Dr H. Scholze for his valuable discussions. Some other aspects of organic modification of glass structures will be discussed in the paper given by him. Moreover, the author thanks the coworkers who could not be cited in the references, the Minister für Forschung und Technologie of the Federal Government of Germany and many industrial companies for supporting this work.

### References

- [1] W. Noll, *Chemie und Technologie der Silicone*. 2. Aufl. (Verlag Chemie, Weinheim, 1968).
- [2] M.G. Voronkov, V.P. Mileshevich and Y.A. Yuzhelevskii, *The Siloxane Bond* (Consultants Bureau, New York and London, 1978).
- [3] H. Dislich, *Angew. Chem.* 83 (1971) 428.
- [4] R. Roy, *J. Amer. Cer. Soc.* 52 (1969) 344.
- [5] K.S. Mazdiyasi, R.T. Dolloff and J.S. Smith, II, *J. Amer. Cer. Soc.* 52 (1969) 523.
- [6] S.P. Mukherjee and J. Zarzycki, *J. Mater. Sci.* 11 (1976) 341.
- [7] B.E. Yoldas, *J. Mater. Sci.* 12 (1977) 1203.
- [8] K. Kamiya and S. Sakka, *Res. Rep. Fac. Eng. Mie Univ.* 2 (1977) 87.
- [9] M. Nogami and Y. Moriya, *J. Non-Crystalline Solids* 37 (1980) 191.
- [10] G. Carturan, V. Gottardi and M. Graziani, *J. Non-Crystalline Solids* 29 (1978) 41.
- [11] S. Sakka and K. Kamiya, *J. Non-Crystalline Solids* 43 (1980) 403.
- [12] J.D. Mackenzie, *J. Non-Crystalline Solids* 48 (1978) 1.
- [13] H.C. Gullledge, *US Patent* 2 512 058, 20.6.1950.
- [14] K.A. Andrianov, in: *Organic Silicon Compounds* (State Scientific Publishing House for Chemical Literature, Moscow 1955).
- [15] K.A. Andrianov and A.A. Zhdanov, *J. Polym. Sci.* (1958) 513.
- [16] H. Schmidt, O. v. Stetten, G. Kellermann, H. Patzelt and W. Naegele, *Proc. Radioimmunoassay and Related Procedures in Medicine*, Vienna (1982) p. 111.
- [17] H. Schmidt, G. Tünker and H. Scholze, *DP* 30 11 761, 20.3.1980.
- [18] H. Schmidt, H. Scholze and A. Kaiser, *J. Non-Crystalline Solids* 63 (1984) 1.
- [19] G. Philipp and H. Schmidt, *J. Non-Crystalline Solids* 63 (1984) 283.
- [20] H. Schmidt, G. Philipp and C.F. Kreiner, *Ger. Offen.* 31 43 820, 11.5.1983.
- [21] C.J. Brinker et al., *J. Non-Crystalline Solids* 63 (1984) 45.
- [22] H. Scholze, H. Schmidt and H. Böttner, *Ger. Offen.* 29 29 969, 29.1.1981.
- [23] A. Kaiser and H. Schmidt, *J. Non-Crystalline Solids* 63 (1984) 261.
- [24] H. Schmidt, *Organically Modified Silicates by the Sol-Gel Process*, *Materials Research Society Symp. Proc.*, Vol. 32 (Elsevier, New York, 1984).