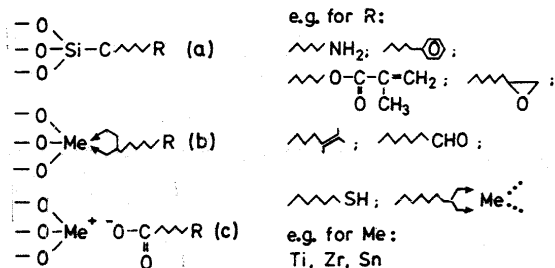


1. Introduction

The basic "construction principles" for inorganic polymers like glasses are network forming units like the $(\text{SiO}_4)^{4-}$ tetrahedron or analogous components which are linked to a three-dimensional network by sharing corners. The properties defined by this principle are well known: Hardness, brittleness, high temperature processing, high T_g values and low free volumes. Almost the opposite can be observed in organic polymers. For example, in hydrocarbons, the structure building units are $\equiv\text{C}-\text{C}\equiv$, $\equiv\text{C}-\text{O}-$ or $\equiv\text{C}-\text{N}=\text{}$ groupings which are linked together to polymeric chains by chemical (not melting) processes and a linear chain is formed in the first step which has to be crosslinked to get threedimensional networks. As a result, the polymers usually are soft, low temperature processing is possible, and the desired elastic or thermoplastic properties can be achieved. The free volume is high due to the organic chain movement and T_g 's generally are low. Figure 1 compares the T_g regimes of the two groups of polymers based on the Cp consideration. There might be an overlap with very special compositions.

The question whether it is possible to synthesize inorganic polymers with organic modification and the route how to realize this has been discussed elsewhere (1-23). In addition to this other principles seem to be possible or have been already realized:

- penetrating porous glass or porous gels by organic monomers and polymerize them (24).
- penetrating inorganic polymer precursors into silicones (23)
- synthesizing independent inorganic-organic interpenetrating networks (25)
- linking organic groupings to an inorganic backbone in various ways, as shown in the following scheme 1.



Scheme 1 - Models for linking organic groupings to inorganic backbones. (a): covalent bond to Si; (b): complex formation to a metal atom, e.g. Zr/acetylacetonates; (c): ionic bond to an organic acid (salt formation).

Organically Modified Ceramics as New Glass-like Materials

H. Schmidt

In this paper, only the models (a) and (b) will be discussed.

2. Scope of properties of the inorganic-organic polymers

2.1 STRUCTURES

In figure 2 some structural models are described. One can distinguish between some basically different structures.

Organics can basically act as inorganic network modifiers and they can do that in two different ways. They can be crosslinked directly to the organic network via a chemical bond or they can be entrapped as molecules into an inorganic network, thus modifying it by creating a chemically or physically different site (a). Or they can act as network formers, e.g. if polymerizable ligands are used (5) (b), which can be polymerized by themselves or with organic monomers. The structure model (c) can be considered as a variation of (b), and, of course, all three principles can be used in one and the same material.

For the realization soft chemistry methods have to be used for the synthesis of the organic backbone since melting together plastics and glass is hardly possible due to the low thermal stability of organic polymers and miscibility problems. Various precursors like $(\text{R}'\text{O})_n\text{SiR}_{(4-n)}$ ($n=2,3$, for R see scheme 1) are commercially available, and it is possible to introduce organics via the sol-gel method into inorganic polymeric materials. Due to the reaction rate differences and the different chemical nature of the monomers and oligomers during the sol-gel processing (equation 1), chemistry has to be carried out very carefully in order to avoid phase separation. Therefore, special procedures like the CCC process (19,20) have been developed.

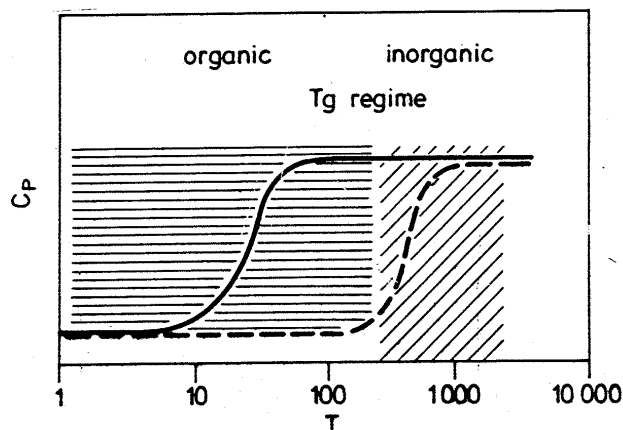


Fig. 1 - Main T_g regimes of inorganic and organic polymers.

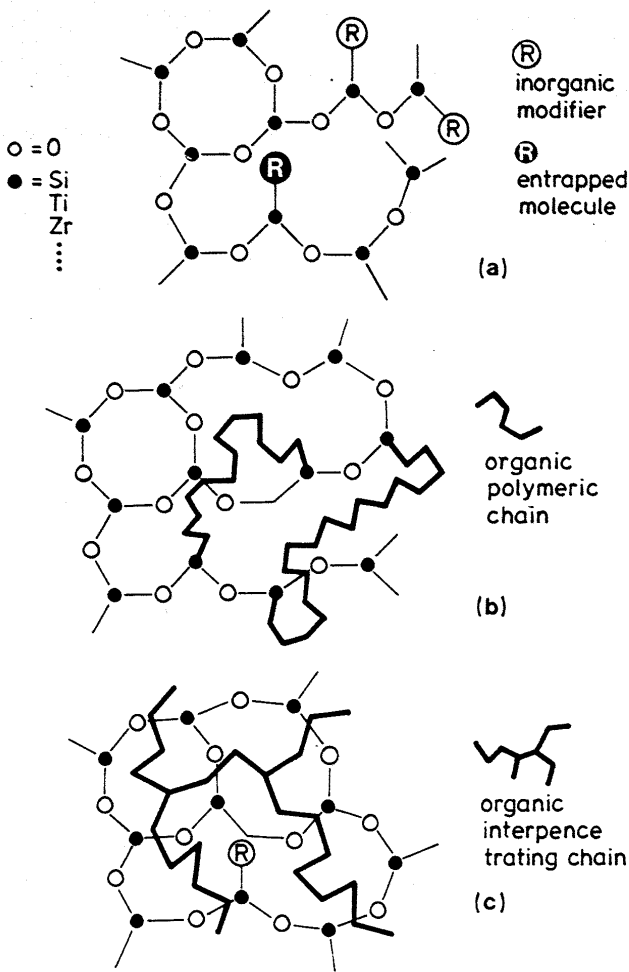
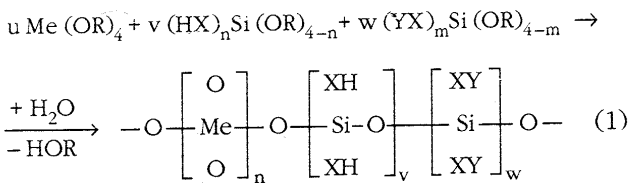


Fig. 2 - Structure models of organically modified ceramics:
a) organics as network modifiers
b) organics as network formers
c) organics as independent networks.

Structural analysis by LAXS of the X-ray amorphous materials suggest medium range order structures as demonstrated on a model substance in the system $\text{TiO}_2/\text{SiO}_{3/2}$ -epoxy (26), as shown in figure 3.



X z. B. $-\text{CH}_2-$, $-\text{C}_6\text{H}_4-$

Y z. B. $-\text{NH}_2$, $-\text{CHO}$, $-\text{COOH}$, Vinyl, Epoxy, Methacrylat

As shown in (27), phase separation can occur if chemistry is not carried out in a suitable way but phase separation (liquid liquid immiscibility) can be introduced if desired for achieving special properties.

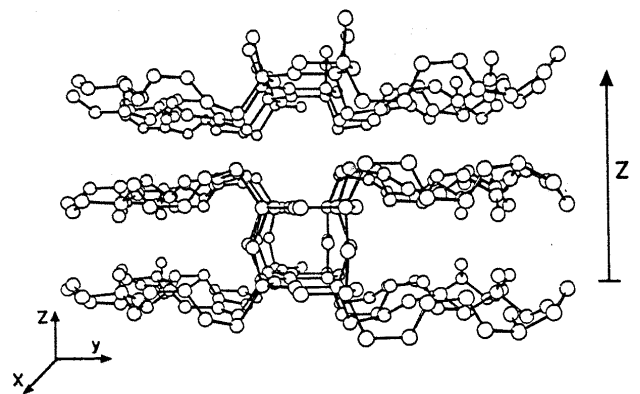


Fig. 3 - Structural evolution of a composition 30 TiO_2 /70 $\text{SiO}_{3/2}$ -epoxy (mole-%) by LAXS after (26).

2.2 PHYSICAL PROPERTIES

The investigation of the surface hardness was carried out by a modified Erichsen test (20). In this test (scratching over a surface with a Vickers diamond), values distinctly superior to common plastics like PMMA and CR 39 (a "scratch resistant" eye glass lens polymer) and even glass are received. This is due to a good compromise between hardness and elasticity. The taber abrader test shows only slight differences to plate glass surfaces. The mechanical data of the materials are given in (20) and show a strong influence of the inorganic heteroatom. The strength increases with $\text{Si} < \text{Zr} < \text{Ti} < \text{Al}$.

The T_g values range from -50°C up to 200 (in some special cases to 300°C). They depend on the degree of crosslinking and the type and number of organic groups per inorganic network forming unit (X). In figure 4, the dependance of T_g on the number X is demonstrated.

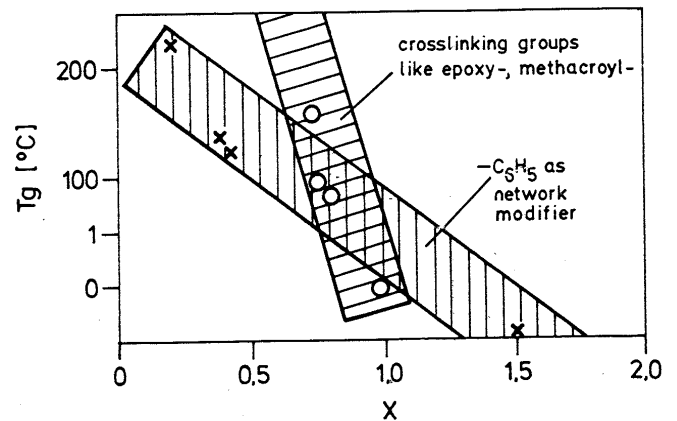
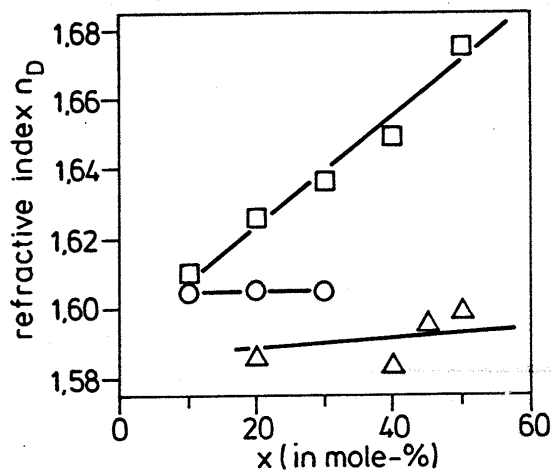


Fig. 4 - T_g values as a function of number of organic groupings.



The effect of concentration of $M(OR)_4$ ($M = Ti, Zr$) in different ORMOSIL systems

□ : $(100-x) Ph_2Si(OH)_2/x Ti(OEt)_4$

○ : $(100-x) Ph_2Si(OH)_2/x Zr(OPr)_4$

△ : $(80-x) Ph_2Si(OH)_2/x Zr(OPr)_4$

20 epoxy silane

Fig. 5 - n_D as a function of composition.

The influence of the organic groups is different. High phenyl group contents lead to thermoplastic materials with very low T_g values. Crosslinking groupings lead to higher T_g values. The materials can be prepared fully dense, with high transparency. The variation of the refractive index of epoxy and phenyl group containing materials is shown in figure 5.

In this diagram, the influence of the central atom and the addition of an organic crosslinking agent (GMD = glycidyl methacrylate) is shown. Whereas Zr concentration variations do not affect n_D , it rises sharply with increasing Ti contents (20).

The density of the materials range from 1.35 to 1.65 and this indicates the strong influence of the organic groupings on the free volume which is higher than the arithmetic mean from a "physical" mixture of the pure inorganic and organic compound would suggest. The inorganic network arranges in a more open structure. In addition to this, the materials are brittle, they break "glass-like" and the strength is relatively low. Summarizing, one can say that the new materials can be considered as new glasses.

3. Examples for applications

3.1 SCRATCH RESISTANT COATINGS

A scratch resistant coating has been developed for CR 39 eye glass lenses with a compromise between hardness and elasticity, specially adapted to the physical properties of the CR 39 (20,28). The coating shows a perfect adhesion to the surface, can be cured at 90 to 120°C and additionally outfitted with vapor deposited antireflective coating without losing its scratch resistance. Other examples are the protection of printed circuit board master copies on glass plates (the photo emulsion containing side has to be protected from mechanical damage during the photo copying process) and the protection of highly polished soft metal surfaces (aluminium, brass, copper). On glass surfaces, this type of coatings shows a strengthening effect by flaw healing.

3.2 FUNCTIONAL MATERIALS

With organics, chemical reactivities can be introduced into the bulk or the surface of the glasses. An active coating has been developed for the immobilisation of antibodies for an immunochemical analysis of hormones (3) as an inside coating for glass tubes. For SO_2 determination, a sensitive system has been synthesized, the permittivity constant of which changes by SO_2 adsorption. The system can be used as coating on an interdigitated capacitive structure for SO_2 monitoring (18). Hydrophilic materials can be achieved by glycol group incorporation, as realized with contact lens materials (5). This type of material can be applied as coatings, too.

3.3 MICROELECTRONICS

Due to the high temperature resistance and excellent dielectric properties, a coating for metal core technology for electronic substrates has been developed (29). A variation of this material was developed for sealing glass containers or glass plates by thermal and UV curing. These materials can be applied as photosensitive coatings to be structured e.g. by LASER writing.

3.4 COLOURED COATINGS

The incorporation of organic dye molecules into sols (e.g. TiO_2 , SiO_2 , TiO_2/SiO_2) leads to intensive colours due to the high coefficient of extinction ($\epsilon \approx 10.000$ l/mole-cm). If thermally stable phthalocyanines are used, the sol-gel coatings can be cured up to 300°C. This

leads to intensively coloured coatings with thicknesses of 0.1 to 0.5 μm which have mechanical properties similar to the glass surface and good chemical stability.

4. Conclusions

The glass-like inorganic-organic polymers have properties between inorganic and organic glasses. Structural aspects justify to consider them as real glasses. Due to the possibility of incorporating functional compounds, the materials have a high potential for new applications in connection with "glass and light".

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