

*Section 6. The sol-gel glass process***ORGANIC MODIFICATION OF GLASS STRUCTURE****New glasses or new polymers?**

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The introduction of organic components into glass structures is possible by sol-gel techniques and leads to hybrid materials. The question whether these materials are more likely glasses or organic polymers is discussed. Different data show that the inorganic network structure governs important properties such as brittleness, hardness, or homogeneity. Other properties, such as density, free volume, or thermal stability depend on the organic groupings. Summarizing one can say that organically modified glasses are more like inorganic glasses than organic polymers.

1. Introduction and general considerations

Glass structure always has been a matter of interest in glass research. In opposition to crystalline materials, the amorphous glass structure allows far more variations compared to the well organized crystalline state. These variations depend on a variety of parameters such as composition, raw materials, melting history, cooling rate, or annealing procedure. Depending on the composition, the rate of approaching the thermodynamically stable state, the "crystallization rate" is very different. Therefore, in some systems, e.g. $\text{TiO}_2 \cdot \text{SiO}_2$ or $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, it is very difficult to obtain crystal-free glasses by conventional melting techniques and as a consequence, inhomogeneities are formed. The degree of inhomogeneity in glasses is extremely important and can be technologically exploited, e.g. in phase-separated glasses, where liquid-liquid immiscibility occurs (for example in the system $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$). Different types of inhomogeneities can be distinguished:

- inhomogeneities by crystallization
- inhomogeneities by phase separation
- inhomogeneities by composition variation
- inhomogeneities by inclusion of impurities.

Composition variation, in general, is due to insufficient homogenization during melting. Inclusion of impurities can be on a macroscopic scale,

but if a chemical reaction takes place, the impurities can lead to structural variation and can modify the glass structure. Examples are oxynitride glasses where N_2 is introduced as an "impurity", leading to a change of the glass structure and to new properties. Another example is carbon. Carbon can be introduced into glasses to a rather high extent and changes structure and properties, too. It is a matter of consideration if one defines a $\equiv \text{Si}-\text{N} =$ bond in a glass structure as an inhomogeneity or a variation of structure. Randomly distributed structural variations, in general, are considered as homogeneous network variations. An interesting question arises: to which extent can glass structures be modified without losing their random distribution, an indispensable parameter for the definition of the glassy state.

Another type of glass, glassy polymers, can be obtained very seldom as pure glasses. In most of them crystalline areas are present or are formed as a consequence of ageing. This is due to the high free volume of the polymers, which allows a chain movement and rearrangement of structure. Since it is very difficult to introduce modifying groups based on organic molecules by conventional techniques (due to the low thermal stability of organics) other preparation techniques have to be used. One of these are sol-gel techniques since they allow the formation of inorganic polymeric networks by low-temperature wet chemical techniques where

organics can be kept stable. The aim of this study was to investigate to which extent glass structure can be modified by organic groupings and how these modifications affect important parameters such as homogeneity but also technically relevant questions such as hardness or brittleness.

2. Results

The sol-gel route for the preparation of inorganic glasses has been described in numerous publications [1-12]. Methods for the incorporation of organics into sol-gel derived glass are described in refs. [13,14]. The process of formation of inorganic sol-gel glasses undergoes the steps of sol formation, gel formation, ageing, drying, and densification by heat at temperatures close to T_g , except for very thin films. The densification step becomes necessary since, due to the three-dimensional network formed by condensation, a porous microstructure is formed and for further densification temperatures around the network softening point are required. Figure 1 gives a schematical description.

In case of organics included in the gel, the inorganic network has either to be widened or the pores have to be smaller or they are lacking completely (fig. 2). In the latter case, shrinkage should decrease substantially or, in other words, the materials should reach their final density at lower temperatures compared to the "inorganic" T_g .

In a former paper it was shown that it is possible to synthesize sol-gel derived monoliths with organics included with remarkable sizes [15]. The materials are prepared by a sol-gel synthesis from $Ti(OEt)_4$, $Si(OEt)_4$, $(RO)_3Si$ -epoxy and $(RO)_3Si$ -methacryl and are crosslinked by epoxy

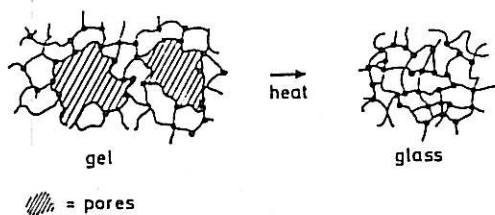


Fig. 1. Gel-to-glass transformation: shrinking and decrease of porosity.

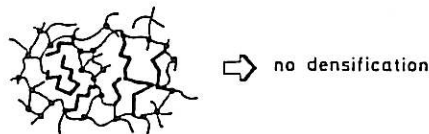


Fig. 2. Lack of substantial densification in organically modified glass structures if pores are filled by organics.

and methacryl polymerization. They can be moulded after partial condensation and polymerization in a viscous state and show a surprisingly *low shrinkage* after curing at 130°C of only 5-6 vol.%. Epoxy-free materials show similar results. This small shrinkage underlines the above hypothesis of structure where organic groupings are filling the space between inorganic chains.

The samples are of *high transparency*. Light scattering is lower than 0.1%, indicating high homogeneity. *Nitrogen adsorption* (BET) does not show any porosity. A *glass transition temperature* cannot be detected at temperatures below the decomposition temperature of the organic network. The samples are fairly *brittle* and the *surface hardness* measured by an indentation scratch test (a Vickers diamond is scratched over the surface and the loading at which the first visible scratch can be observed is used as a surface hardness measure) shows values up to 50 g (PMMA 1-2 g, PC < 1 g). Structural investigations [16] by large angle X-ray scattering (LAXS) indicate *no long-range order*. This result indicates clearly properties which are glass-like. One could conclude that the modification of the glass structure by organics directly linked to the silica atom does not change the glassy character of these materials.

LAXS experiments and the low light scattering indicate further that a high degree of homogeneity exists, underlining again the glassy state of these materials. In opposition to inorganic glasses and in accordance with sol-gel glasses, the homogeneity has to be obtained by chemical synthesis and not by melting. Therefore, special precaution has to be employed, since the sol-gel reaction rate differences of the different precursors are remarkable. Hydrolysis and condensation rate differences can be easily controlled by the use of in situ water generating reaction, thus avoiding H_2O

the compositions in table 1. This means that the incorporation of organics leads to a free volume more typical for organic polymers than for glasses. The optical properties of various modified glasses are shown in fig. 3. The optical properties are close to those of various optical glasses, but tend into the direction of organic polymers.

The high degree of homogeneity (fig. 4) is shown in a high resolution STEM micrograph. This material is prepared by the CCC method with a composition according to table 1, first line. Within the resolution of the instrument (~ 10 nm) no phases or separation effects can be detected.

Another example is shown in fig. 5. This example represents a glass made from Si-epoxy silane, Si-methacryl silane and hexamethylen-diamine (HMD) as crosslinking agent. Phase separation takes place at Si-epoxy: HMD $\leq 1:1$ (Si-epoxy:Si-methacryl = 1:1) indicating a lower degree of crosslinking when the HMD exceeds that amount for the 1:1 ratio. The two phases have about the same Si content as measured by high resolution EDAX. One can conclude that in this system, the immobilization of the different phases can be carried out by organic crosslinking, if proper conditions are applied, but also that phase separation can be introduced. The samples are prepared by hydrolysing Si-epoxy silane to a slightly viscous liquid in ethanol/H₂O/HCl, adding the Si-methacryloxy silane, continuing hy-

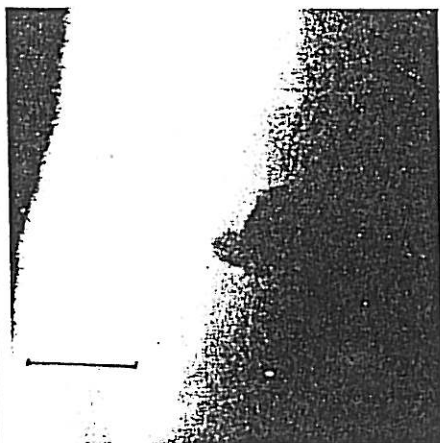


Fig. 5. STEM micrograph of modified glass (composition see text) with phase separation; bar = 50 nm.

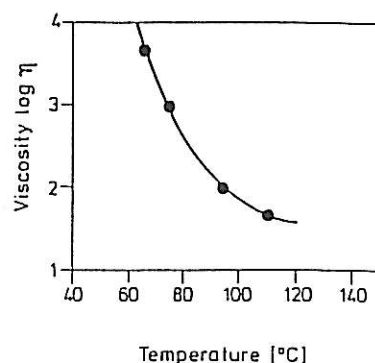


Fig. 6. $\log \eta/T$ plot of a modified glass. SiO₂:C₆H₅SiO:Me-ViSiO = 25:60:5 (molar ratio).

drolysis and condensation, removing the solvent and HCl, then adding the amine.

Organic groupings can not only act in a structural sense but also can have functional properties. This flexibility allows the introduction of properties into modified glasses which cannot be obtained in pure inorganic glasses. A few examples, therefore, will be given.

Chemical reactivity can be obtained by incorporation of organofunctional groups such as $-\text{NH}_2$ or $-\text{CHO}$ [18] or $-\text{NR}_2$ (adsorption of SO₂) [19]. Adhesive properties and thermoplasticity can be obtained by introduction of the $=\text{Si}(\text{C}_6\text{H}_5)_2$ and MeViSi = groups (Me = methyl, Vi = vinyl) [20].

The thermoplastic behavior, which is very similar to that of glasses, but is only shifted to lower temperature, is shown in fig. 6. The behavior is reversible and the materials are stable up to 280°C, which is low for glasses, but high for common polymers.

3. Conclusions

Organically modified glasses exhibit properties which lead to the conclusion that they can be considered as glasses. Differences to pure inorganic glasses are the density that indicates a high free volume. The range of properties is very wide since the organic modification not only changes structure but also the chemical behavior. As a consequence of this large variety of possibilities not too many systematic data are available.

But these data show clearly that the materials behave more like inorganic glasses, even with high contents of organic groupings.

The author wants to thank Dr. Hörth, Dr. Raether, Dr. Rose, and Mr. Zieder for their experimental work and helpful discussions and the Bayerisches Staatsministerium für Wirtschaft und Verkehr for financial support.

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