

A FIRST LOOK AT THE OPTICAL PROPERTIES OF ORMOSILS

Birgit LINTNER, Nanning ARFSTEN and Helmut DISLICH

Schott Glaswerke, Mainz, FRG

Helmut SCHMIDT, Gottfried PHILIPP and Bernhard SEIFERLING

Fraunhofer Institut für Silicatiforschung, Würzburg, FRG

1. Introduction

The optical properties of glasses and plastics, especially the n_d-v_d -diagram, the optical region are well known [1] whereas those of organic modified silicates (ormosils) are unknown.

The interesting aspect of the optical region of ormosils is given by the fact that these materials (as mixtures of inorganic and organic components) have two possible ways to affect the region. On the one hand, as with glasses, very many elements can be incorporated as inorganic network formers (e.g. SiO_2 , ZrO_2 , TiO_2) and as network modifiers (e.g. Na_2O , MgO , BaO), while on the other hand organic network formers such as polymers chains of many types and length (e.g. with aromatic and aliphatic monomer units) and organic network modifiers (e.g. Si-CH_3 , $\text{Si-C}_6\text{H}_5$) are also possible. Thus the extent of possible variation is almost boundless, and justifies our natural curiosity to investigate what effects in the optical region can be expected from the approach. However, it was clear from the beginning that the effects achieved to do not have to be as dramatic as the possibilities would imply from the Lorentz-Lorenz calculation of the hypothetical products. The following natural restrictions apply:

- the products have to be “makeable”, from a practical point of view;
- they must be produced in a transparent form;
- in the case of multicomponent systems, the nature of the chemical binding is by no means clear;
- it can happen that the components are not properly bound to one another, but are con-

nected by mixed networks or enmeshed with another;

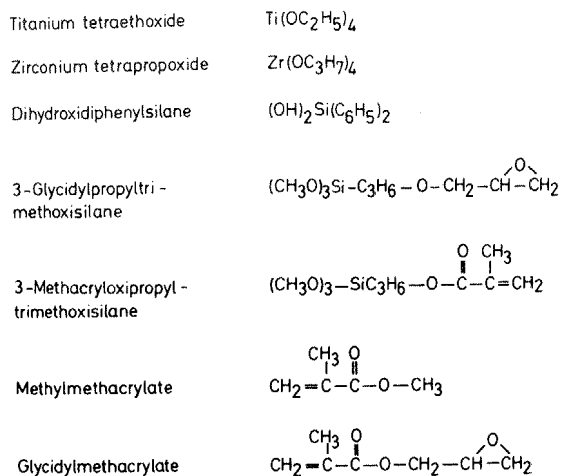
- the resulting density affects the optical region of the product considerably.

The above text has defined our initial aims and starting models, and we have chosen the title of this report to reflect the fact that it is truly only a first look at the optical properties of ormosils. Accordingly, in the following we will now report our first findings with only a minimum attempt at explanation.

2. Several starting materials and one (possible) structure of a final product

Fig. 1 shows several starting materials. The following principle is important. The organic groups remaining in the product (i.e. not hydrolysed) are always connected to the silicon by a Si-C bond, since all other inorganic bonds to carbon in the reaction mixture are more or less readily hydrolysed. The functionality can be inferred from fig. 2.

The latter compound can copolymerise with methyl-methacrylate and glycidyl-methacrylate, and furthermore each species can copolymerise with every other one, so that the final structure of fig. 3 is feasible. This is only a working hypothesis, since we do not know at present (as mentioned above) how the individual components are actually linked together. This representation employs inorganic and organic network formers and network modifiers shown in more detail in fig. 4. The



Some solution- and auxiliary products:
toluene, ethanol, acetone, acetic acid, water, hydrochloride acid,
dicyclohexylperoxidicarbonate

Fig. 1. Some precursors for preparing transparent heteropoly-siloxanes.

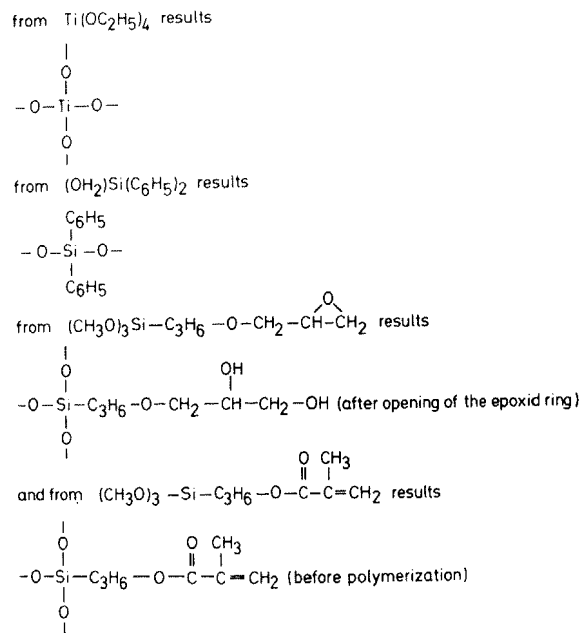


Fig. 2. Some hydrolysis and condensation products.

organic network formers can also be of long chain type. The organic network modifiers are Si-methyl and Si-phenyl groups. We will show in the next section that these principles can be used to pre-

pare ormosils in a tailor-made fashion with respect to optical data such as the n_d-v_d relationship. In principle, all three of the major polymerisation reactions can be involved: polycondensation,

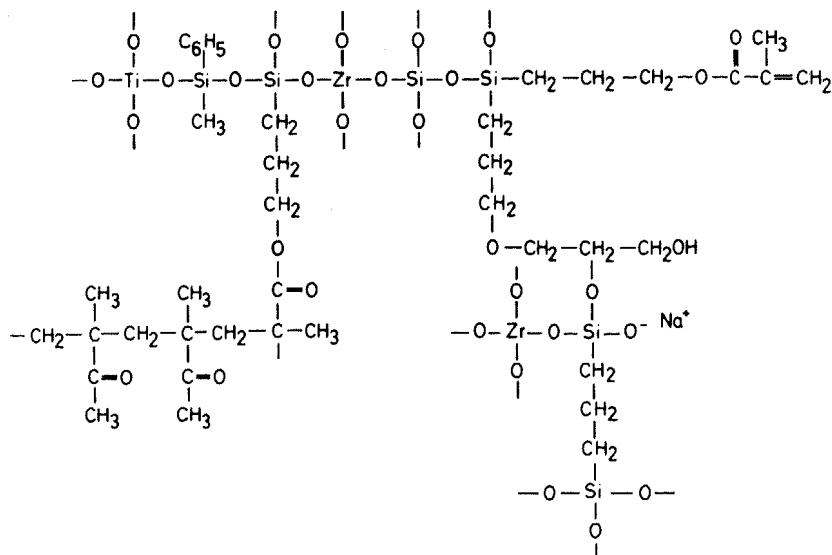


Fig. 3. Possible network of ormosils.

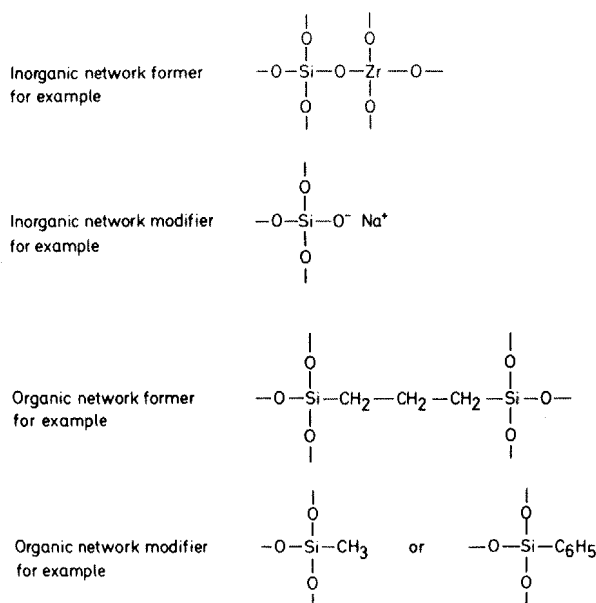


Fig. 4. Network formers and network modifiers in ormosils.

polymerisation, polyaddition, but, as noted, we cannot as yet be sure of the details.

3. Several transparent ormosils

The n_d - v_d area is very large. We have already reported our investigations of the bottom left area (pure plastics), far below the glass limits [2,3], so we now decided to concentrate on the upper right area. As a first step, the Lorentz-Lorenz calculations were carried out, then suitable starting materials sought, reaction conditions were investigated, and the resulting products isolated and measured.

3.1. Lorentz-Lorenz calculations

The basis is given by the Lorentz-Lorenz equation

$$R_M = \frac{n^2 - 1}{n^2 + 1} \frac{M}{d} \quad (1)$$

When the structure and molecular weight are known then this equation allows us to calculate the refractive index from the molar refraction

term R_M , the molecular weight and the density. The molar refraction is a term which expresses the sum of the refraction contributions of the individual components, and thus of the individual chemical bonds involved. Groups with easily polarisable electrons increase refraction, and the inclusion of less polarisable groups produces the opposite effect. The values of n_C , n_d and n_F can thus be calculated, and these are then used for a first calculation of the Abbe number using

$$v_d = \frac{n_d - 1}{n_F - n_C} \quad (2)$$

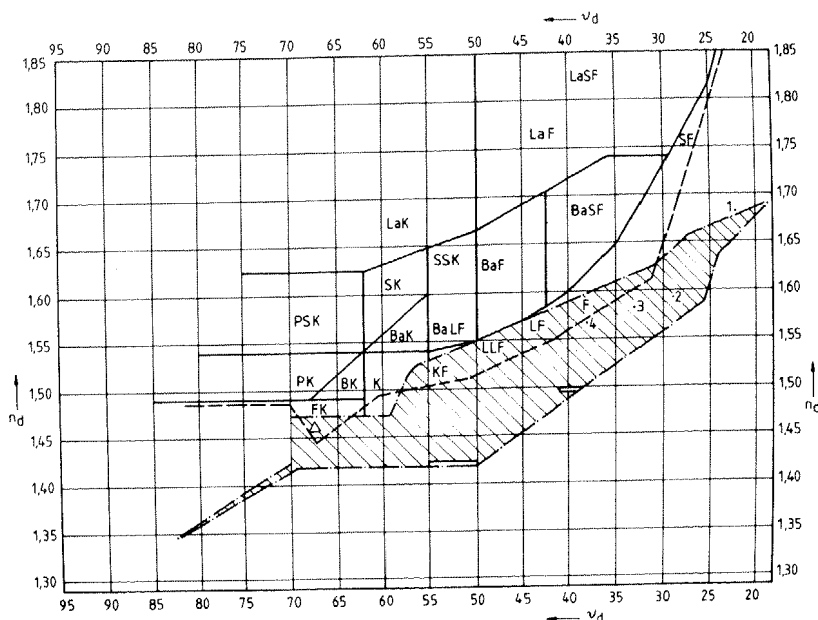
The values so obtained promised a considerable degree of flexibility in the n_d - v_d relationship, and this was then confirmed by experiment. We observed a remarkably good correspondence between measured and calculated values, whereby the predictive power is limited by the unknown value of the density.

3.2. The production of transparent Ormosils

The starting materials of fig. 1 were dissolved in alcohol and 1 mol of the mixture (different compositions) was heated at 50°C for 30 min. The reaction mixture was then hydrolysed with the stoichiometric equivalent of 0.1 mol aqueous HCl and then heated under reflux for 1 h to complete the reaction. The volatile solvents and reagents were distilled off and the viscose residue poured into polyurethane moulds. The hardening of the samples was carried out by slow heating to 120°C.

3.3. Several ormosils in the n_d - v_d diagram

Fig. 5 shows several compositions in the n_d - v_d -diagram. Materials with both a high content of aromatics and TiO_2 have high refractive indices and low values of the Abbe number (example 1, table 1). If TiO_2 is replaced by ZrO_2 , then the refractive index is reduced, while the Abbe number rises (example 2, table 1). The incorporation of aliphatic compounds in the polymer system allows further variation in the results produced (examples 3 and 4, table 1). This table serves to demonstrate the variation of the refractive index and the Abbe

Fig. 5. Some compositions of ormosils in the n_d-v_d diagram.Table 1
Different compositions of Ormosils

Compositions (mol%)	n_d	v_d
1 40Ph ₂ SiO/60TiO ₂	1.68	23
2 50Ph ₂ SiO/50ZrO ₂	1.59	28
3 40Ph ₂ SiO/40ZrO ₂ /20 Glymo	1.58	33
4 40Ph ₂ SiO/40ZrO ₂ /20 Glymo + 30 GMA	1.57	38

number over a wide field on the use of varied oxide, aromatic and aliphatic components.

4. Summary and perspectives

As the title of this paper indicates, we have taken only a "first look" at the optical properties of ormosils. Nevertheless, in this short summary of the preparation and properties of these materials we have endeavoured to show that the refractive index and the Abbe number can be made-to-order with a high degree of success. In this respect the Lorentz-Lorenz equation is a very useful tool for the prediction of the direction (and possibly for the limits) of the effects, but the absolute values

cannot be calculated exactly in advance, since the density is a parameter which must be experimentally measured on the product itself.

It is remarkable how often transparent products are obtained. We also noticed that a relatively small amount of organic component gives the product a surprising degree of the mechanical properties of a plastic. On a second glance this result is not so surprising, since "monomethylpolysiloxane" ("mono-methylated silica glass" gives a similar result [1-3], values of the mechanical properties (surface hardness, Young's modulus) being typical of plastics. Thus the classification of the ormosils as intermediates between the organic and inorganic polymers is certainly supportable from the standpoint of their structure and is also in accord with the control possible in the design of their optical data. For instance, it could be interesting and useful to raise the refractive index of a polymer by the incorporation of TiO₂ or ZrO₂ instead of introducing a C-Hal unit (Hal = Cl, Br or J). However, as shown above, the mechanical properties tend to those of the plastics even when a high percentage of inorganic oxide is present.

There can be little doubt that the field between organic and inorganic polymers will be increasingly investigated in the future. Ormosils are only one possibility among several. A second way would involve the polymerisation of different monomers in the pores of SiO₂-monolithics [4] derived from the sol-gel procedure. Hereby fully transparent materials result even where great differences exist between the refraction of the host and the implanted material, which naturally depends on the size of the pores. A future comparison between the optical (and other) properties of the products of this type of "physical mixing" and the products

described in the present paper ("chemical mixing") will be very interesting, under conditions of constant chemical composition.

References

- [1] H. Dislich, *Angew. Chem. Int. Ed. Engl.* 18 (1979) 49.
- [2] H. Dislich and A. Jacobsen, DBP 14 94 872 (1965) Jenaer Glaswerk Schott & Gen., Mainz, FRG.
- [3] H. Dislich and A. Jacobsen, *Angew. Chem. Int. Ed.* 12 (6) (1973) 439.
- [4] J.D. Mackenzie, Final Technical Report No. AD-A127 404, Univ. of California, Los Angeles (1982).