

Inorganic-organic composites (ORMOCERs) for optical application.

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### ABSTRACT

Organically modified ceramics (ORMOCERs) have been prepared with respect to optical applications. The investigations show that materials can be synthesized with interesting properties for a variety of potential applications. They can be used as hard coatings for the protection of optical polymers, e.g. CR 39 or fluorescent dye containing PMMA. The incorporation of dyes leads to active optical matrices, e.g. fluorescent coatings and the introduction of components with high refractive increments to refractive index numbers  $n_D \leq 1.68$ . For microoptic applications, materials suitable for photolithographic patterning or direct laser writing have been developed.

### 1. INTRODUCTION

For optical applications two types of materials have gained importance: glasses and polymers. Glasses are characterized by high processing temperatures and a costly shaping and finishing process, polymers can be processed at lower temperatures but show a poorer performance with respect to optical properties like  $n_D$  or  $D'$ , as shown in Fig. 1.<sup>1</sup> In addition to optical data distinctly differing from those of inorganic glasses, the mechanical surface properties of polymers exclude many practical applications. Therefore, protective coatings tailored for polymers have to be developed which are suitable for the mechanical and optical data of polymers and which provide sufficient surface protection. ORMOCERs can be located between glasses and polymers, as described in 2.2. They are hybrid materials the properties of which should be able to be adapted to a variety of requirements. The basic principles of ORMOCER synthesis has been described elsewhere.<sup>2-4</sup> Similar principles have been used by Wilkes<sup>5</sup> to synthesis high refractive index composites. First optical ORMOCER materials have been synthesized for contact lens applications.<sup>6</sup> A multicomponent system with various specific properties such as high oxygen permeation, intrinsic hydrophilicity and high mechanical strength was developed on the basis of the ORMOCER principle.

The question arises how far ORMOCERs can be used as a principle for materials for various optical applications. In this paper, data of ORMOCERs, as they have been developed in the Fraunhofer-Institut

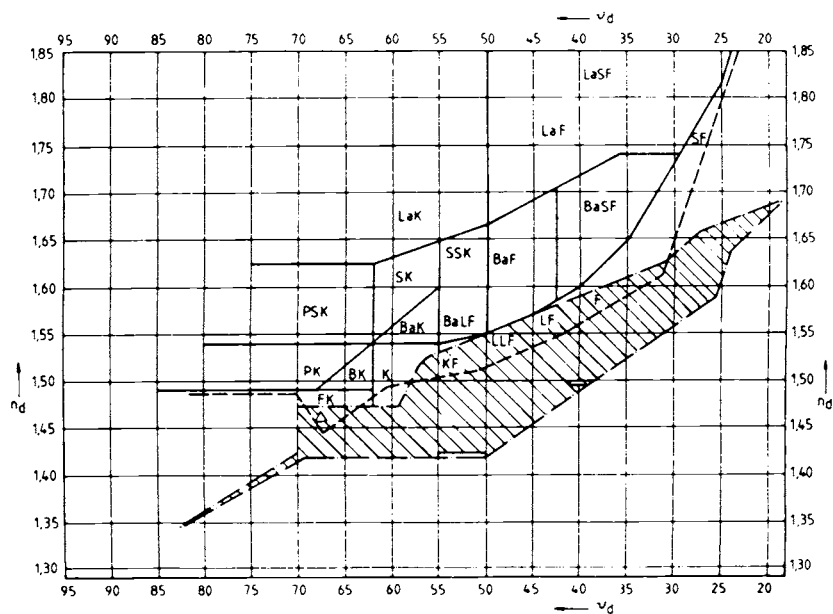


Fig. 1. Properties of optical glasses and polymers in the  $n_D/v_D$  plot. The written symbols refer to optical glasses of Schott Glaswerke company. The full circles refer to ORMOCERS (see also Chapter 2.2.).

für Silicatiforschung, are presented for an overview over the state of the art.

## 2. RESULTS AND DISCUSSIONS

### 2.1. Protection of surfaces

If materials from organic polymers are used for high performance optical components, the surfaces have to be protected from mechanical impact. The coating materials have to be adapted to the thermal expansion and to the modulus of elasticity of the substrate. As shown in <sup>7</sup>, the thermal expansion coefficient  $\alpha$  of ORMOCERS can be varied within a wide range (Fig. 2) and easily be adapted to a polymeric substrate.

Other requirements for polymer coatings are low curing temperatures and high abrasive resistance (compared to the substrate). The question of "surface hardness" is a difficult one and strongly depends on the practical stress conditions. In many cases, "soft" materials (e.g. rubber tires) under special circumstances can show a better performance than "hard" materials. As experiments have shown, the incorporation of inorganic ("brittle") components into a polyethylene oxide polymer<sup>8</sup> can increase the abrasion resistance of the polymer substantially. These materials are composed of  $TiO_2$ ,  $SiO_2$



The low curing temperature of only 90 - 100 °C can be explained by the sol-gel condensation which takes place by simply evaporating the solvent and the fact that the organic polyethylene chain leads to sufficient matrix relaxation behavior to densify these materials at the indicated low temperatures. One important point is, that due to the active curing (the final "infinite" network is generated by condensation during the curing step), low molecular weights (500 - 1000 D) can be used in the coating laquers. Suitable viscosities can be obtained by high solid contents (up to 80 wt.%, which is rather high compared to polymer based laquers). As a consequence, high coating thicknesses can be obtained by one step processes (5 - 10  $\mu\text{m}$ ). The abrasion resistance of the coatings is very good and haze measurements after a standardized taber abrader treatment (200 rev.) show about 2 % (flat glass  $\approx$  1 %, CR 39 uncoated 20 %). The UV stability of the coating is fully sufficient for eye glass requirements. Due to the  $\text{TiO}_2$ , the material shows an electronic conductivity of about  $10^{-5}$ - $10^{-6}$   $\sigma$ , which is sufficient to be used as a transparent electrode material.

For higher UV stabilities,  $\text{TiO}_2$  has to be replaced by  $\text{Al}_2\text{O}_3$  as network formers. The preparation of the Al-containing materials is described in detail in <sup>10</sup>. The materials are prepared from (I)  $(\text{RO})_3\text{Si}(\text{CH}_2)_2\text{OCH}_2\text{-}\overline{\text{CHCH}_2\text{O}}$ , (II)  $\text{Al}(\text{OR})_3$ , and (III)  $\text{C}_6\text{H}_5\text{Si}(\text{OR})_3$ ,  $\text{CH}_3(\text{CH}_2)_2\text{Si}(\text{OR})_3$  or  $\text{CH}_2=\text{CHSi}(\text{OR})_3$  alternatively.  $\gamma$ -aminopropyltriethoxysilane can be added as adhesion promoter for PMMA, analogueous to the  $\text{TiO}_2$  coatings. The scratch resistance of this type of coatings is high and in the same range as the  $\text{TiO}_2$  coatings. Depending on the type of substituting group in (III), various properties can be obtained: propyl leads to low  $\text{H}_2\text{O}$  take-up and these coatings are very stable against moist conditions (weathering for 14 days at 100 % r.h. and 40 °C). The ORMOCER coatings directly employed to the sputtered metal layers<sup>11</sup> provide sufficient chemical and mechanical protection (Fig. 4).

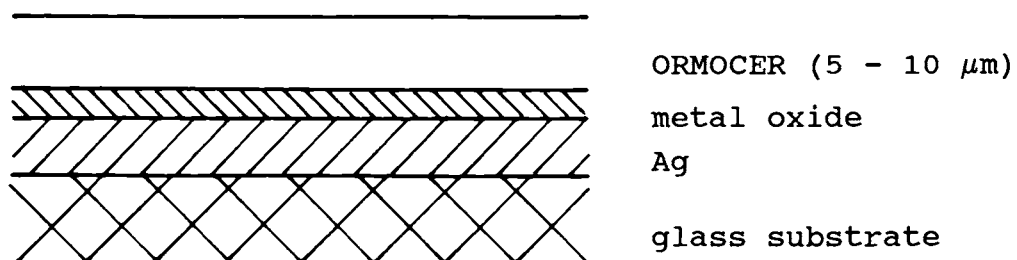


Fig. 4. Metallization protection ORMOCER coating.

The introduction of  $(\text{RO})_3\text{Si}(\text{CH}_2)_2\text{OCOCH}(\text{CH}_3)=\text{CH}_2$  instead of (III) leads to photocurable compositions if photocatalysts (e.g. IRGACURE 184, Ciba Geigy company) are added. All these types of coatings can be prepared with homogeneities suitable for optical coatings.

If necessary, the coatings can be prepared even with thicknesses up to 100  $\mu\text{m}$ . This was developed for coloured coatings with fluorescent dyes included. As shown in <sup>12</sup>, dyes of the perylene type can be incorporated and the system can be used for solar collectors. The incorporation of organic components into such systems is almost unlimited. NLO molecules can be introduced as shown by Dunn<sup>13</sup> and Prasad<sup>14</sup>.

## 2.2. Bulk materials

The first optical bulk materials have been developed for contact lens applications.<sup>6</sup> In this case, rods (10 cm in lengths, 2.5 cm in diameter) have been molded from viscous precursors and photocured by MMA polymerization). The rods were cut into blanks and mechanically machined to contact lenses.

In other experiments,  $\text{C}_6\text{H}_5$  containing silanes were combined with  $\text{TiO}_2$  or  $\text{ZrO}_2$  by condensation of  $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$  and  $\text{Ti}(\text{OEt})_4$  or  $\text{Zr}(\text{OPr})_4$  as precursors (50 % toluene as solvent).  $\gamma$ -glycidyloxypropyl silane and methacrylic acid glycidylester (MGE) were added in order to reduce the brittleness of the systems. In Fig. 5 the  $n_D/\nu_D$  diagram of the systems without MGE and in Fig. 6 the effect of MGE on various material data is given. The results are in accordance with Lorentz-Lorenz calculations, if the correct densities are used.

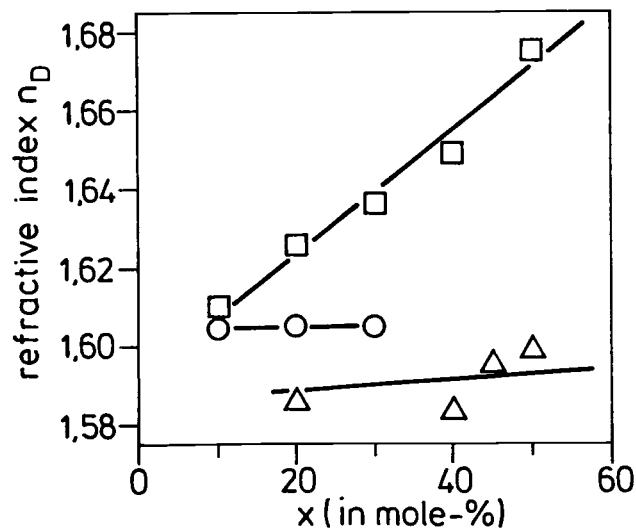


Fig. 5. Effect of  $\text{M}(\text{OR})_4$  on the refractive index of ORMOCERs.  
 $\square$   $(100-x)\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2/x\text{Ti}(\text{OEt})_4$ ;  $\circ$   $(100-x)\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2/x\text{Zr}(\text{OPr})_4$ ;  
 $\Delta$   $(80-x)(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2/x\text{Zr}(\text{OPr})_4/20\gamma$ -glycidyloxypropyl triethoxysilane (molar ratio of precursors).

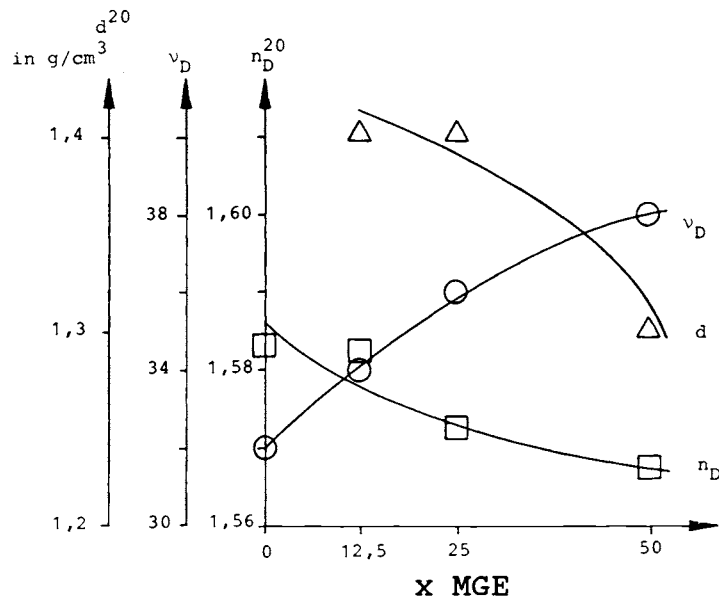


Fig. 6. Density,  $v_D$  and  $n_D$  of ORMOCERs as a function of the addition of MGE in the system  $40(C_6H_5)_2Si(OH)_2/40Zr(OPr)_4/20\gamma$ -glycidyoxypropyl triethoxysilane/ $x$ MGE; molar ratio).

The results show that  $n_D$  values between 1.57 and 1.68 can be obtained with ORMOCERs. Lower values can be easily prepared, too. For higher values, further optimization is necessary. As shown in <sup>7</sup> the density of ORMOCERs does not increase with increasing content of inorganic components as it should be expected from the density of the crystalline phase. For example, a 40 wt.% containing glycidyoxypropyl based ( $\equiv$  POE chain containing) ORMOCER, which is expected to have a density of about  $2.5 \text{ g/cm}^3$  only shows a value of about 1.6. This means that the ORMOCER is not a ceramic polymer composite in a conventional sense (a physical mixture of crystalline  $ZrO_2$  and the polymer), but a composite in which the  $ZrO_2$  plays the role of a threedimensional network former similar to a threedimensional cross-linking organic group.

The materials can be prepared as coatings and as bulk products. Most of them show a very good abrasion resistance and can be used as protective transparent coatings, too.

The incorporation of inorganic ions into ORMOCERs is possible, too. As described in <sup>15</sup> the incorporation of  $V^{4+}$  ions into a  $\gamma$ -glycidyoxypropyl silane based ORMOCER leads to coatings with an effective absorption band in the near infrared for solar protection. If  $ZrO_2$  or  $TiO_2$  are substituted by  $Al_2O_3$ ,  $n_D$  values down to 1.35 can be obtained.

### 2.3. Patternable ORMOCERs

For microoptic or integrated optic applications, the formation of geometrical structures is an important feature. Therefore, ORMOCERs for photolithographic or laser writing processes have been developed. The synthesis of these materials is described elsewhere.<sup>16</sup> The process consists of three steps, the preparation of an ORMOCER precursor for coating techniques with high homogeneity and transparency, the lithographic step after coating and the development step of the patterns and final curing.

As photopolymerizing step the crosslinking methacryloxy groups bond to Si were chosen. For achieving thick coatings with a one step coating, the solid content of the precursor should be as high as possible. This can be obtained by a solvent-free processing using modified silanes only. The slowly reacting silanes also allow the preparation of stable coating laquers with a shelf live of several months. If network formers with high reactivity with respect to condensation, e.g.  $\text{Al}(\text{OR})_3$  is used, patternability can be provided, but the shelf live is reduced drastically.<sup>17</sup>

A suitable system consisting of organo silanes and  $\text{SiO}_2$  was developed from  $\gamma$ -glycidyoxypropyl trimethoxysilane :  $\gamma$ -methacryloxypropyl trimethoxysilane : vinyl trimethoxysilane :  $\text{Si}(\text{OEt})_4 = 39 : 39 : 18 : 4$  (molar ratio) by refluxing the precursors for several hours with about 50 % of the water necessary for complete hydrolysis. By spin-on techniques substrates can be coated up to about  $13 \mu\text{m}$  thickness in a one step process. The coatings can be polymerized, if about 0.1 wt.% photoinitiator (e.g. IRGACURE 184) is added. If a laser writing technique is used, as shown in <sup>16</sup> and <sup>17</sup>, the width of the patterns depends strongly on the laser intensity. After light exposure, the patterns were developed either with diluted NaOH or acetone.<sup>16</sup> Under these conditions, the ORMOCER is sufficiently polymerized but not to be redissolved. The width increases with laser exposure time which can be attributed to light reflection from the interface and chain propagation into "dark" areas. Fig. 7 shows an example of a patterned ORMOCER.

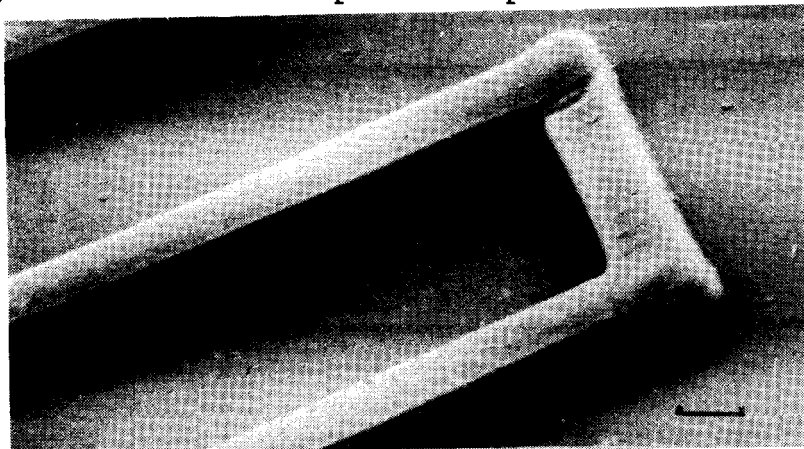


Fig. 7. Developed ORMOCER patterns received by laser writing  $600 \text{ W/cm}^2$ , scanning rate:  $2 \text{ mm/s}$  (bar refers to  $10 \mu\text{m}$ )

This technique allows to generate dielectrics for SMD techniques for microelectronics as well as wave guides for optics. In combination with active components (e.g. inorganic ions or organic molecules with special functions) the ORMOCERS open interesting perspectives.

#### 4. CONCLUSIONS

As the data have shown, ORMOCERS with interesting optical properties and a potential for optoelectronic applications can be prepared. As a consequence of the high number of compositions and processing parameters, most of the discussed systems are not yet optimized. Three groups of materials already have been developed to a state which clearly shows the application potentials: transparent hard coatings, transparent bulk materials and materials for patterning. The combination with active components will be an interesting task for future work.

#### 5. ACKNOWLEDGEMENT

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