PROCESSING AND OPTICAL PROPERTIES OF INORGANIC-ORGANIC COMPOSITES

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INTRODUCTION

Use of tailored materials in integrated optics, laser materials, data storage, or communication technologies is increasing. There is a need for active and passive materials to meet a desired function, and the tendency is to integrate several specific functions into the same type of material. These may be either operational functions or combinations of processing and operational functions (e.g., coatings with nonlinear properties and functions allowing patterning by photolithographic techniques). In general, composites are required for these types of multifunctional materials. For optical applications, the dimensions of the composite components have to be either on a molecular level or in the nanometer range. Dimension control is easily solved in systems where the function is attributed to molecules dissolved in a matrix (e.g., lanthanide ions in glasses or dyes in polymers), but use of a polymer as matrix produces problems of diffusion stability. This can lead to aggregation of dyes and loss of desired optical properties due to a change of optical properties of dye molecules from
lack of stability of the system. In other systems like ceramic–ceramic, ceramic–
glass, or ceramic–polymer systems, the control of dimension is essential for
optical applications. Within ceramics, this can be obtained by nucleation or
crystallization control. If ceramics are prepared by sol–gel techniques (e.g.,
coatings), a variety of nucleation control mechanisms exists to control phase
size. [1]. For ceramic–polymer composites, nanosized ceramic powders have to
be used, which leads to processing difficulties if the conventional route of mixing
polymers with fillers is followed. Moreover, availability of agglomerate-free
nanosized powders is poor, and smaller dimensions down to the molecular level
cannot be obtained this way. For these cases, the synthesis of polymers in the
polymerization or polycondensation step with organics and inorganic compo-
nents both present have the potential of appropriate size control, as already
shown [2–5].

In this chapter, the sol–gel route of synthesizing organically modified
ceramics (ORMOCERs) as described elsewhere [6,7] and its potential for
optical application are reviewed; general possibilities of size control are shown
and some examples using these approaches are given.

METHODS FOR HOMOGENEITY CONTROL
IN ORMOCER SYSTEMS

General sol–gel methods for synthesizing ORMOCER materials are described
elsewhere [5–10]. The basic principles for these multicomponent systems
include a chemical reaction control to keep phase separation on a level as low as
possible. Therefore, it is worthwhile to think about linking the inorganic and
organic components chemically in the molecular or oligomeric state where the
precursors are not yet hydrolyzed or condensed. Figure 64.1 shows some
chemical principles for linking inorganic to organic components. Therefore,
covalent, ionic, and coordinative bonds can be used.

The organics act as a network former if nonreactive groups (e.g., —CH₃,
—C₂H₅, and —C₆H₅) or nonpolymerizable functional groupings (like
—(CH₂)ₙ—NR₂, —COOH, or others) are used. Polymeric chains can be formed
by use of double-bond-containing groups (vinyl, methacryl, or other olefine
groups), for example, or epoxides. The copolymerization of organic monomers
leads to an extension of organic chains [8]. The cocondensation of additional
inorganic network-forming components ("pure" inorganic or organically modi-
ﬁed) requires adequate means to suppress reactivity-based phase separation,
which was demonstrated with the synthesis of scratch-resistant coatings from
(RO)₃Si(CH₂)₃OCH₂—CH—CH₂—O/SiO₂/TiO(Et)₄ or Al(prop)₃ [10–11].
In these cases, the successful route was to create reactive OH groups (≡TiOH,
≡AlOH) that then react more or less randomly with ≡Me—OR groups, thus
forming mixed-bond polymers without detectable phase separation down to the
level of nanometers, as shown elsewhere [12] (Fig. 64.2a). These intermediate
species are aggressive and very rapidly consume ≡Me—OR groups. Another
route is the immobilization of inorganic precursors [e.g., Zr(iprop)$_4$, which forms colloids very easily after water addition]. The aggregation process can be successfully suppressed by catching these species with “elastic” bonds, as indicated in Fig. 64.2b. This immobilization step into an organic network to be formed can be carried out, for example, by methacrylic acid, (MMA) as shown in Fig. 64.2b [13], and finally, chemical traps, where an inorganic component is inside a complex structure (Fig. 64.2c) [14].

**TYPES OF ORMOCERS FOR OPTICAL APPLICATIONS**

**Thermoplastic Materials**

As shown in the literature [15, 16] use of the $\text{C}_6\text{H}_5\text{Si}\text{C}_6\text{H}_5$ unit keeps the chain length of cocondensates with alkoxides small (3–5000 D) and results in soluble and thermoplastic materials. Due to their excellent adhesion to glass surfaces, they can be used as seals, e.g., fiber-to-chip coupling, for architectural glazing [15] or even for the protection of medieval stained glass windows, a very special “optical” application [17].
create active species to react with slowly reacting species

\[ \text{activate} \quad \text{reactants} \rightarrow \text{products} \]

example:

\[ \text{Ti(OR)}_4 \rightarrow \text{H}_2\text{O} \rightarrow \text{RO(OR)}_2 \rightarrow \text{RO-SiOR} \rightarrow \text{homogeneous viscous liquid} \]

\[ \text{Zr(OR)}_4 + 2 \text{HOOC-CH}_2 \rightarrow \text{Zr-CH}_3 \rightarrow \text{very stable monolithic materials; IR-data} \]

\[ \text{MMA} \rightarrow \text{polymerization yield with monofunctional MMA=80\%} \]

\[ \text{Cu} \quad \text{Si} \quad \text{Si} \]

\[ \text{NH} \quad \text{CH}_3 \quad \text{NH} \]

\[ \text{H}_2 \quad \text{H}_2 \quad \text{H}_2 \]

\[ \text{CH}_2 \quad \text{H} \quad \text{CH}_2 \]

Figure 64.2. Various routes to overcome homogeneity limiting rate differences of precursors in multicomponent systems: (a) Formation of highly reactive species; (b) immobilization of alkoxydes within a polymeric system from methacrylic acid and methylmethylacrylate; (c) formation of coordinatively ordered structures.

Photocurable ORMOCERS

A survey of curing mechanisms is given in Table 64.1 [18]. The ORMOCER systems allow the photoinitiated condensation of the sol–gel reaction as well as organic polymerization. As shown elsewhere [8], Ti(OR)_4 catalyzes the formation of polyethylene oxide chains for epoxides in the presence of light. In [TiO_4]^4– group-containing transparent ORMOCERs (e.g., contact lens materials [19] and hard coatings [10]), an electronic conductivity of \( \sigma \approx 10^{-5} \) was observed [20], which is substantially larger than in other ORMOCERs (\( \sigma \approx 10^{-12} \)) [16]. A structural model of these materials was developed elsewhere [21] by LAXS indicating a structure with oxygen-coordinated Ti (Fig. 64.3.).

The electronic conductivity can be explained by a Ti defect structure with a defect being “handled” by chain movement (Fig. 64.4). This type of charge
TABLE 64.1. Photocuring Mechanisms of ORMOCERs: Polymerizing Ligands

<table>
<thead>
<tr>
<th>Structure</th>
<th>Reaction ( R \cdot R ) (thermal, UV)</th>
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<tbody>
<tr>
<td>( \equiv \text{Si} - \text{CH}_2 \cdots \text{CH} = \text{CH}_2 )</td>
<td>( R^+ R^- (UV)^b )</td>
</tr>
<tr>
<td>( \equiv \text{Si} - \text{CH} = \text{CH}_2 + \text{H}_3\text{C} - \equiv \text{Si} )</td>
<td>( R \cdot R ), thermal</td>
</tr>
<tr>
<td>( \equiv \text{Si} - \cdots \text{CH} = \text{CH}_2 + \text{MMA} )</td>
<td>( R \cdot R )</td>
</tr>
<tr>
<td>( \equiv \text{Si} - \cdots \text{CH} - \text{CH}_2 + \equiv \text{Si} \equiv + \text{NH}_2\text{R} \cdots )</td>
<td>( R^+ R^- )</td>
</tr>
<tr>
<td>Ti, Zr, Al</td>
<td>+ \text{MMA} ( R \cdot R )</td>
</tr>
</tbody>
</table>

*Polymerization, mechanism polycondensation, polyaddition.

*If \( R^+ = \text{H}^+ \), photo activated condensation becomes possible; \( R \) = radical, ion.

Transport mechanism has been indicated in so-called ORMOLYTes by neutron-scattering and cyclovoltammetric measurements [22].

The system can be prepared as highly transparent coatings and can be used as transparent electrodes despite their low conductivity since they can be applied in thicknesses up to 50 \( \mu \text{m} \).

The photocuring ability can be used in various ways for optical purposes, such as patterning (e.g., photolithography or laser writing) [23–25]. Another use is embossing of prepolymerized ORMOCERs during photocuring, which leads to sharply edged patterns due to the low shrinkage of the ORMOCER system [26].

Schematics of embossing and laser writing of ORMOCERs are shown in

System: \( \text{TiO}_2 / \equiv \text{Si} - \equiv \text{SiO}_2 \)

![Diagram](attachment:image.png)

*Figure 64.3. Structural model of Ti-containing ORMOCERs [19].
Figs. 64.5a, b. The scanning electron microscopy (SEM) micrograph of an embossed film is shown in Fig. 64.6.

**Doped ORMOCERs**

If prepolymer (liquids or soluble materials) are prepared [8, 10, 15, 16], dopants can be added very easily. In the case of inorganic ions, complex formation is an adequate means to dissolve metal salts (e.g., Pt) very homogeneously. Copper and Ni can be incorporated into amniue structures with NH\_2—CH\_2—CH\_2—CH\_2Si(OR)\_3 (I) or NH\_2—CH\_2—CH\_2—NH—CH\_2—CH\_2—Si(OR)\_3 (II) as ligands. Structures shown in Fig. 64.2 can be obtained. In the case of Cu, an intensive blue color is obtained showing the typical spectrum of the Cu tetrammine complex. Nickel, Fe, and Ag can be incorporated by similar reactions. In methyl methacrylate modified ORMOCERs, dyes have been incorporated into prepolymer serving as a high-molecular-weight solvent (5–1000 D). Table 64.2 summarizes some dyes incorporated into ORMOCERs. The optical spectra indicate no aggregation and are similar to those of the dissolved dyes. Photochromism can be obtained, too. These experiments indicate the enormous variability of the ORMOCER system.

**Figure 64.5.** Schematics of ORMOCER patterning: (a) embossing; (b) laser writing.
CONCLUSIONS

The ORMOCER system shows properties of interest for optical applications. These are mechanical properties, processing properties (densifying temperatures between 50 and 150°C), photocuring properties enabling pattern formation by photolithography, laser writing and embossing, and the possibility of doping with inorganic ions as well as with organic dyes. However, questions concerning structures, structure formation mechanisms, and relations of structure to properties still need to be answered. The enormous stabilization of lasing dyes in ORMOCER systems [27] leads to the question about the basis (matrix effect)

<table>
<thead>
<tr>
<th>Dye</th>
<th>wt %</th>
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<tbody>
<tr>
<td>Fluoresceine</td>
<td>0.029</td>
</tr>
<tr>
<td>Eosine</td>
<td>0.068</td>
</tr>
<tr>
<td>523 Photo</td>
<td>0.017</td>
</tr>
<tr>
<td>Disperse red</td>
<td>0.030</td>
</tr>
<tr>
<td>Acridine orange</td>
<td>0.028</td>
</tr>
</tbody>
</table>

*From ref. 26.
*Approximate values.
*Phototropic dye.
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and how this can be optimized. ORMOCER systems are at its infancy with respect to optical application, but the potential is promising.

ACKNOWLEDGMENT

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REFERENCES