Embossing of Ormocers

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1. Introduction

Integrated optics require special material properties with respect to low cost component fabrication. The manufacturing of glass components, for example requires several time-consuming steps including ion exchange (1). For polymer channel waveguides, laser ablation techniques have been developed with high-performance surfaces to reduce light scattering and optical losses (2).

But polymers exhibit in opposition to glasses some structure based disadvantages as low T_g and limited stability concerning poled incorporated NLO organic dyes. Therefore, the use of thermoplastic organic polymer materials suitable for low cost embossing techniques will be critical and it is necessary to reinforce the organic structure in order to increase their stability. Based on these considerations, it was of interest to investigate the potential of organically modified ceramics of the ORMOCER type as stable materials for embossing. These materials are synthesized through the sol-gel route (inorganic backbone) and, in addition to this, can be polymerized if polymerizable groupings are present (3, 4, 5). There are several possibilities to connect the inorganic backbone to organic groupings or chains. A convenient link is the $\equiv$Si-C$\equiv$ bond, since Si can form stable $\equiv$Si-O bonds, too, at the same atom. Another link can be provided by coordinative bonds, which is of importance for sol-gel processing, if it is possible to connect inorganic network formers like Al, Ti or Zr to organics. it is well-known, that β-diketones form bonds to alkoxides of these elements (6), but there are not enough data about stability of these bonds to be applied as a material "construction" element.

In order to design materials to be used as planar or channel waveguides and to undergo an embossing step, several stringent requirements have to be fulfilled, such as tailoring of the refractive index, low optical loss, high T_g or network stability, exact reproduction of the embossing matrix (near net shaping), high mechanical surface quality. There is a variety of contradictions from these requirements. Near net shaping with inorganic sol-gel materials is difficult due to the high amount of shrinkage during the firing processes required to obtain dense materials (7, 8). Low temperature embossing requires soft materials (e.g. organics) which exhibit the disadvantages mentioned above. Therefore, it is interesting to which extent these disadvantages can be overcome by ORMOCER systems. Thus, ORMOCERs have to be developed with tailorable refractive indices, high T_g preferrably to be built up during the embossing step and high structural homogenity to keep optical losses as low as possible.

2. Experimental

The process of synthesis for ORMOCER materials with Zr as an important inorganic structural element is described elsewhere (9). This synthesis was developed for a direct LASER writing process, using a focused LASER beam as light source. For embossing, the process had to be modified to produce soft films to be able to be embossed. Fig. 1 shows the general process necessary to control homogeneity and visco-
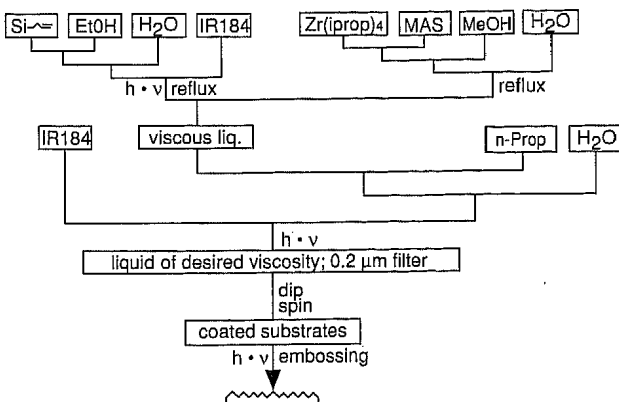

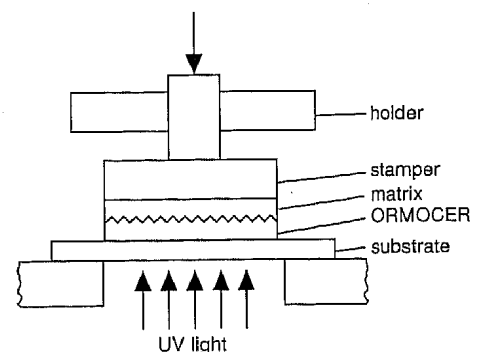Fig. 1 - *Draft of the preparation process of an ORMOCER coating for embossing.*

Fig. 2 - *Draft of the embossing device.*

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sity. For embossing, various matrices were used as grids or optical arrays.

For curing during embossing fused SiO_2 as an UV transparent substrate was used. In Fig. 2 the draft of the embossing step is shown.

For the photo initiated polymerization step, Irgacure 184 (Ciba Geigy) was used as initiatior. Finally the embossed patterns were cured at 130°C for 1 hour.

3. Results and discussion

In order to tailor the refractive index, Zr was chosen as modifier. In Fig. 3, the influence of type and concentration of the inorganic network formers and n_D is shown (10). Beside Zr and Ti shows a strong influence, too. But with Ti, only yellow wish materials could be obtained.

The introduction of Zr in organic matrices was investigated by Arfsten et al. (11), who used Zr-methacrylate to be incorporated into a variety of organic polymers, but this systems does not show very good surface hardness. Therefore, alkoxides of Zr have
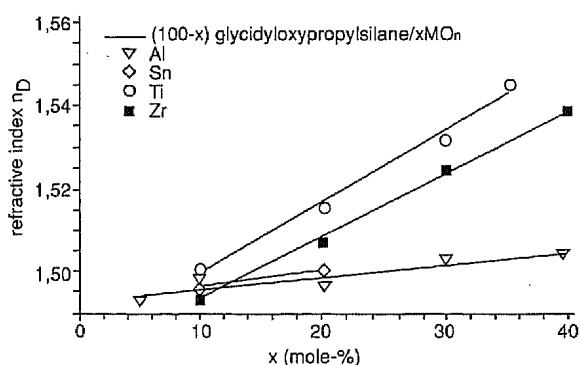
Fig. 3 - *Comparison of the effect of various inorganic components on the refractive index in ORMOCER matrices.*

been used, as described in (12). The reaction of $Zr(OR)_4$ with methacrylic (MA) acid allows the formation of a complex molecule, which coordinates to $Zr(OR)_4$ in two steps, as shown in Fig. 4 (13).

The question arises, whether this complex formation includes at least partly a salt formation (ionic bond) and, in addition to this, whether this bond is stable in a hydrolysis and condensation process. An ionic bond is expected to hydrolyse in an aqueous medium at least partially, as known from salts of weak acids and bases. It is known from (13) that $Zr(OR)_4$ should form chelates with organic acids, but no data about hydrolytic stability are given. The chelate formation

shifts the $>C=O$ frequency of MA from the 1700 cm⁻¹ region into the region below 1600 cm⁻¹ (Fig. 5).

It is remarkable, that no traces of υ_{CO}-MA can be observed in the IR spectrum after H_2O addition, indicating the structures proposed in Fig. 3 to be maintaned during hydrolysis with respect to the chelate
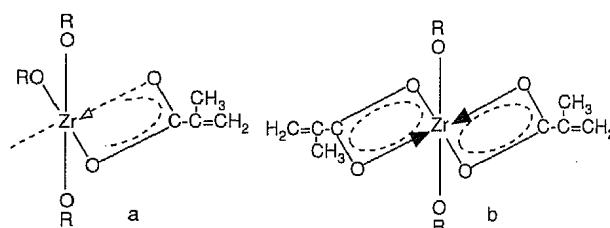
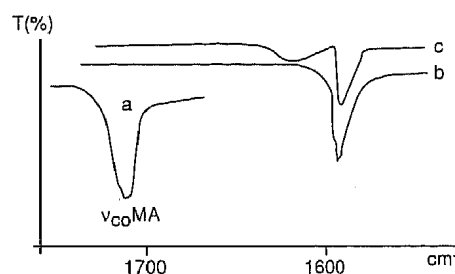Fig. 4 - *Suggested structures for complex formation of Zr alkoxides with MA.*

Fig. 5 - *C_O frequency of MA; a: pure MA; b: after complexation; c: after hydrolysis with Zr $(OR)_4$.*

bonds. ¹³C NMR data support these findings (9). This shows, that the organic acid complexation of $Zr(OR)_4$ provides an interesting means to incorporate Zr into organic matrices, if MA ligands are used to be polymerized with other olefins. Therefore, $(RO)_3Si(CH_2)_3OCO(CH_3)=CH_2$ (MS) were used. MS is used to form an additional inorganic backbone, too. It is of importance to carry out the reaction process according to Fig. 1. After removal of volatile reaction products (solvent, H_2O), the remaining viscosity of the liquid is adjusted with butanol to be suitable for spin or dip coating. After drying, the soft surface can be embossed according to Fig. 2. no traces of phase separation can be detected in the system by electron microscopy. A typical embossed pattern is shown in Figs. 6 a and b.

The embossed structures represent very exactly the shape of the mould. Independent shrinkage measu-
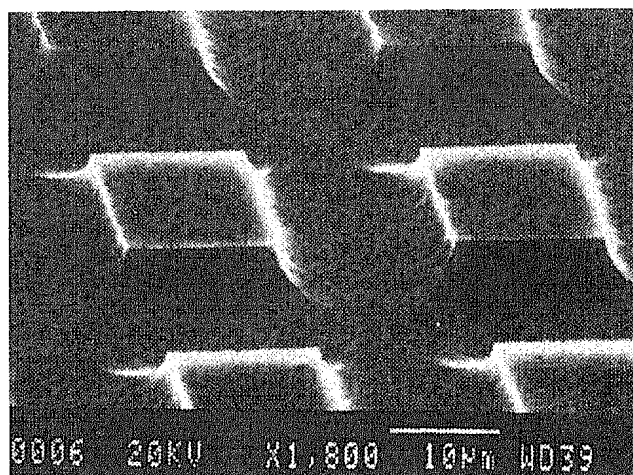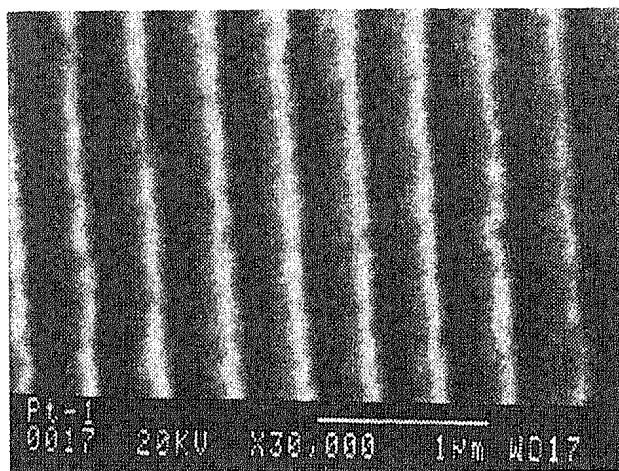
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Fig. 6 - *Embossed patterns; a: by an optical grating; b: by a grid.*

rements show, that the shrinkage of the liquid (non-cured) system to the finally cured system is in the range of ≈ 5 vol.-%. It is expected to be lower from the dried to the embossed film. The edges of the patterns are very sharp and the sides are steep, as one can see in Fig. 6. The surfaces are very mooth. The curing during embossing is carried out by UV irradiation. The time required depends on UV light intensity (some minutes to 15 minutes). After curing the C=C double bond intensity of the acrylate is reduced to about 15% (85% yield of polymerization). First experiments show, that the variety of organic dyes can be dissolved in the system. The optical losses are still in the range of some dB/cm, but this was due to dust particles. Therefore, clean room conditions have to be improved.

4. Conclusions

It is possible to tailor important properties of inorganic-organic composites by chemistry. The coordination of alkoxides with acids seems to be an appropriate means to distribute inorganic components very homogeneously within organic or hybrid matrices.
Of course, this reaction principle has to be improved and extended to other systems in order to show its general usefulness.

5. Acknowledgement

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