ORGANICALLY MODIFIED SILICATES AS INORGANIC-ORGANIC POLYMERS

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1. Introduction
Chemical synthesis of organic polymers is one of the most important types of reactions in chemical industry. It has reached a high level, but still work seems to be necessary to improve organic polymer properties. Especially the low surface hardness limits applications in a considerable number of cases. With respect to this property, inorganic materials, like glass or ceramics are superior to organic materials. It is known that successful attempts are made with different types of composites (e.g. fibre reinforced plastics, filled plastics, laminates, coatings) on so-called macroscopic scale, whereas only few work is done on organic-inorganic composites on a molecular scale.

2. General consideration
Networks of organic polymers are generally based on linear chain, well-defined crosslinked in order to achieve desired properties. Networks of inorganic non-metallic materials generally have a threedimensional highly crosslinked network due to inorganic network formers like the \[ \text{SiO}_4 \] tetrahedron. This results in a high brittleness, typical for glasses and ceramic materials. The question to be raised, how far it is possible to combine these two types of networks. Since glasses and ceramic materials in general have to be processed at high temperature (melting or sintering), other types of synthesis techniques for inorganic networks have to be applied in connection with organic components. Therefore, the so-called sol-gel process [1-5] seems to be a suitable synthesis method. Inorganic networks can be synthesized at low temperature. An example is given in eq. (1) for the synthesis of a sodium-borosilicate glass

\[
\text{Na}_2\text{O} + \text{B(OR)}_3 + \text{Si(OR)}_4 \xrightarrow{+ \text{H}_2\text{O}} \text{NaOH} + \text{B(OR)}_3 + \text{Si(OR)}_4 \xrightarrow{+ \text{H}_2\text{O}} \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{Si}_2\text{O}_5 \quad \text{(gel)}
\]

Whereas the network forming condensation step towards the gel usually occurs at room temperature, the glass transition step requires still medium high temperatures around 70\(^\circ\) C of the inorganic glass.

Silicone synthesis [6] uses the condensation step of \( \text{Si(OR)}_4 \) + HO-Si to \( \text{SiO-Si} \) as a network forming reaction. The polymer backbone therefore is a mainly linear \( \text{Si(O-OR)_2-SiO} \) chain, which is crosslinked in a desired manner. Early work on extending these principles towards the inorganic organic polymers is reported from [7-9] but no systematic investigation on material development has followed. Different construction principles of inorganic-organic polymers are possible: The simplest model is the organic modification of an inorganic backbone by e.g. Si-O-linked organic groupings (Fig. 1a), which act as network modifiers only. In Fig. 1b a model for organically crosslinked network and in Fig. 1c the model of two interpenetrating networks are given.

3. Synthesis principles
A reaction path of inorganic-organic using sol-gel techniques is given in eq. (2)

\[
u \text{Me(OR)}_4 + v(\text{HX}) \xrightarrow{+ \text{H}_2\text{O}} n \text{Si(OR)}_4 + w(\text{XX}) \xrightarrow{+ \text{H}_2\text{O}} \text{Si(OR)}_4 \xrightarrow{+ \text{H}_2\text{O}} \text{Me(OR)}_4 + \text{Si(OR)}_4 + \text{Si(OR)}_4
\]

X e.g. -CH\(_2\)_n -CH\(_3\), -COOH, vinyl, epoxy, methacrylate

Y e.g. -NH\(_2\), -CHO, -COON, vinyl, epoxy, methacrylate

Synthesis in detail is described elsewhere [10-15].

4. Material developments
4.1. Introduction of organic network modifiers
The introduction of organic network modifiers into \( \text{SiO}_2 \) glasses leads to drastic changes of properties. For example, \( \text{SiC}_{1.5} \) glass has a thermal expansion coefficient of about 0.5 \( 10^{-6} \) K\(^{-1}\), monoethoxy-silica \( \text{SiO}_2 \) glass (CH\(_3\))\(_3\) / Si\(_2\)O\(_5\) about 100 \( 10^{-6} \) K\(^{-1}\).

In our investigations the adsorption behaviour of CO\(_2\) as a function of organic modification in porous \( \text{SiO}_2 \) systems was measured. Fig. 2 shows the comparison of three adsorbents, synthesized under equal reaction conditions (hydrolysis and condensation of Si(OC\(_2\)H\(_3\))\(_4\), CH\(_3\)-Si(OC\(_2\)H\(_3\))\(_3\) and NH\(_2\)(CH\(_3\))\(_2\)-Si(OC\(_2\)H\(_3\))\(_3\) (am) in 50 vol.% CH\(_3\)OH with 0.1 M HC\(_1\) and stoichiometric amount of water).

The influence of the modification on adsorption behavior is obvious. The extreme high load at low pCO\(_2\) values can be attributed to a weak dipole-dipole interaction between the aminogroup and CO\(_2\), the relatively high load of CH\(_3\) group containing adsorbents to a hydrophobic interaction. The example demonstrates the influence of structural changes in inorganic polymers by organic modification on selected properties.
4.2. Organic network formers

As indicated above, an additional organic network can be built up by organic polymer synthesis within an inorganic network. The basic principle according to (3) is shown in Fig. 3.

![Diagram of polymerization reaction](image)

The influence of organic strengthening is shown in Fig. 3. Hydrophobic copolymers can be synthesized through condensation of Ti(OH)₄, Si(OH)₄, and epoxy-Si(OH), according to (3). The addition of methacryloyl-Si(OH), according to (3), leads to a remarkable increase in tensile strength.

![Diagram showing increase of tensile strength](image)

5. Conclusion

The combination of inorganic-organic polymers on a molecular level opens an interesting possibility of synthesizing new materials. Organic polymer synthesis and sol-gel-techniques seem to be suitable techniques for this. The field is just at the beginning of its development.

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6. Literature