

by

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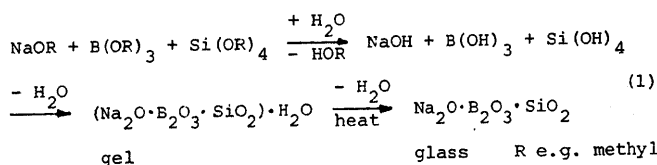
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1. Introduction

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 limitates 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 an interesting question, how far combinations of organic and inorganic materials can help to improve properties of both types of materials. Successful attempts are made with different types of composites (e.g. fibre reinforced plastics, filled plastics, laminates, coatings) on a so-called macroscopic scale, whereas only few work is done on organic-inorganic composites on a molecular scale.

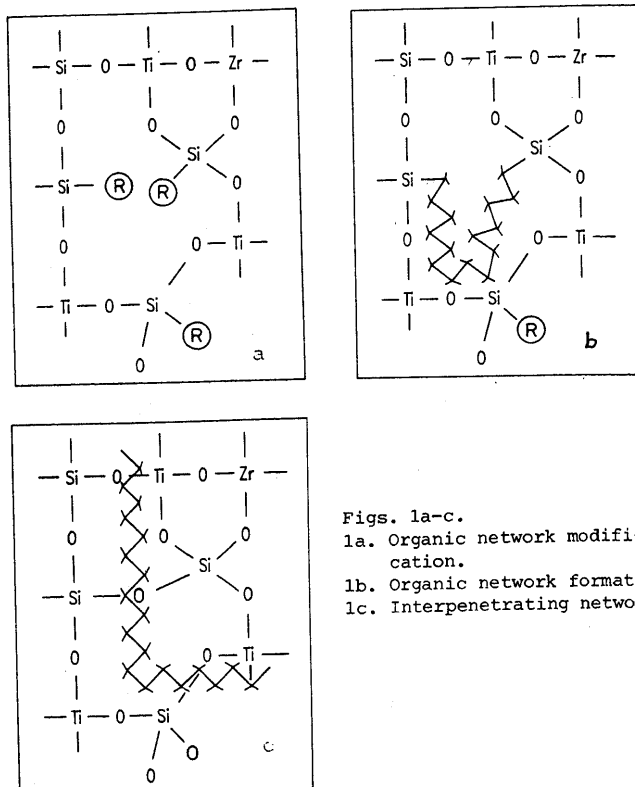
2. General consideration

Networks of organic polymers are generally based on linear type chains, well-defined crosslinked in order to achieve desired properties. Networks of inorganic non-metallic materials generally have a three-dimensional highly crosslinked network due to inorganic network formers like the $[\text{SiO}_4]^{4-}$ tetrahedron. This results in a high brittleness, typical for glasses and ceramic materials. The question has to be risen, 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



Whereas the network forming condensation step towards the gel usually occurs at room temperature, the glass transition step requires still medium high temperatures around T_g of the inorganic glass.

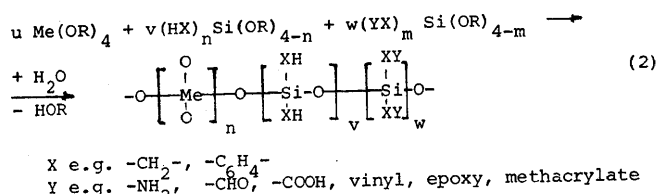
Silicone synthesis [6] uses the condensation step of $\text{SiOH} + \text{HO-Si}$ to Si-O-Si as a network forming reaction. The polymer backbone therefore is a mainly linear $-\text{Si-O-Si-O-Si}-$ chain, which is crosslinked in a desired manner. Early work on extending these principles towards the inorganic 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 of by Si-C -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.



Figs. 1a-c.
1a. Organic network modification.
1b. Organic network formation
1c. Interpenetrating networks

3. Synthesis principles

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



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 SiO_2 glasses leads to drastic changes of properties. For example, SiO_2 glass has a thermal expansion coefficient of about $0.5 \cdot 10^{-6} \text{ K}^{-1}$, monomethyl- SiO_2 glass ($\text{CH}_3\text{SiO}_3/2 \text{ n}$) about $100 \cdot 10^{-6} \text{ K}^{-1}$.

In our investigations the adsorption behaviour of CO_2 as a function of organic modification in porous SiO_2 systems was measured. Fig. 2 shows the comparison of three adsorbents, synthesized under equal reaction conditions (hydrolysis and condensation of $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{CH}_3-\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{NH}_2(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$ (am) in 50 vol.% CH_3OH with 0.1 N HCl and stoichiometric amount of water).

The influence of the modification on adsorption behavior is obvious. The extreme high load at low $p\text{CO}_2$ 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 of inorganic polymers by organic modification on selected properties.

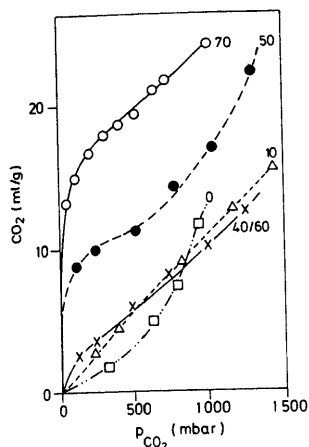
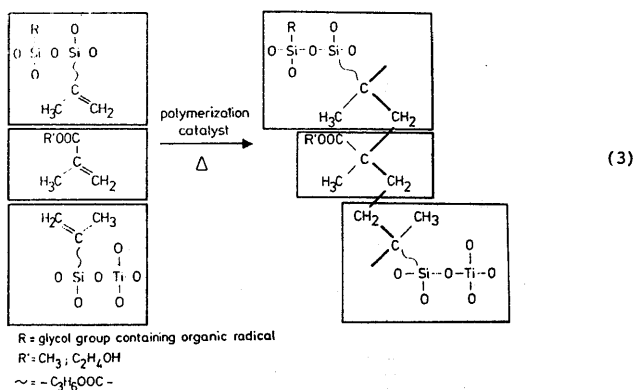


Fig. 2.

Adsorption isotherms of CO_2 on different network modified adsorbents; 70: network former SiO_2 to network modifier (am) ratio (molar): 30:70; 50: 50:50; 10: 90:10; 0: 100% SiO_2 ; 40/60: 40 SiO_2 and 60 $\text{CH}_3\text{SiO}_{3/2}$ (molar); specific surface areas all between 200 and 300 m^2/g .

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 [1] is shown in e.g. (3)



The influence of organic strengthening is shown in Fig. 3. Hydrophobic copolymers can be synthesized through cocondensation of $\text{Ti}(\text{OR})_4$, $\text{Si}(\text{OR})_4$ and epoxy- $\text{Si}(\text{OR})_3$ according to [1]. The addition of methacryl- $\text{Si}(\text{OR})_3$ according to (3) leads to a remarkable increase of tensile strength.

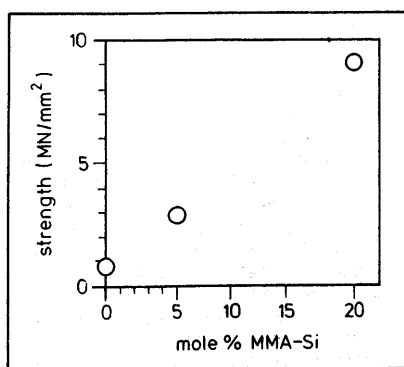


Fig. 3. Increase of tensile strength by methacrylate addition to the polymer system $\text{TiO}_2/\text{SiO}_2/\text{SiO}_{3/2}\text{-R}$;
 R = $-(\text{CH}_3)_2\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2\text{OH}$

The methacrylate-free system is brittle with very insufficient mechanical properties. The reinforced system is scratch resistant (abraser test gives about 2 % haze with the scattered light test; PMMA: 30 to 40 %) and highly hydrophilic (contact angle $< 20^\circ$) surfaces.

4.3. Interpenetrating networks

Sol-gel techniques may be used for building up interpenetrating networks by simultaneous or consecutive synthesis of both types of networks. As an example, an amorphous $-\text{O}-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$ containing interpenetrating network was synthesized by use of a ethyl-vinyl-acetate copolymer dissolved in toluene as liquid phase. $\text{Ti}(\text{OR})_4$ was added slowly, hydrolysis and condensation were carried out through a H_2O vapor pressure controlled atmosphere. The resulting insoluble polymer exhibits a high scratch resistance in the diamond scratch test. Diamond loads of up to 20 g (vickers diamond) do not result in visible scratches (microscope observation); PMMA, epoxides, CR 39: ≤ 1 g).

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

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