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RECEIVED September 1, 1987

Reprinted from ACS SYMPOSIUM SERIES No. 360

Inorganic and Organometallic Polymers

Martel Zeldin, Kenneth J. Wynne, and Harry R. Allcock, Editors

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Chapter 27

Organically Modified Silicates as Inorganic-Organic Polymers

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The combination between inorganic and organic polymeric materials on an atomic scale depends strongly on methods for synthesizing inorganic polymeric networks suitable to the thermal stability of organic materials. The sol-gel process as a "soft-chemistry" method has been proved to be a proper tool for building up inorganic network incorporating organic components. A review over examples for material development and possibilities of tailoring by chemistry using sol-gel techniques in combination with organic components (organically modified silicates) is given.

Novel materials have always played an important role for the development of new technologies. Since the requirement of modern technologies with respect to material properties became more and more specific it was necessary to develop composites: Properties of different types of basic materials have to be combined in order to fulfill these specific requirements. Moreover, natural raw materials, especially in the field of ceramics, could not meet the requirements for a lot of desired purposes (e.g. purity, homogeneity, reactivity), so novel raw materials were developed by chemical synthesis.

One of the most important chemical routes to ceramics is the sol-gel process (1-5) which was proved to open unique new possibilities to improve material or processing properties (e.g. coatings, powders, fibers and even monolithic materials). One of the key steps on the way from the (mono- or oligomeric) precursor to the solid is the polycondensation step, which defines to a great deal the structure of a prepolymer or polymer to be formed and thus influences processing and final material properties essentially. One of the major advantages of sol-gel techniques is the fact that the network forming step of the inorganic polymer is carried out at rather low temperatures in organic or aqueous solutions (compared to classical glass melting or ceramic firing temperatures). This leads to the possibility of incorporating organic components into inorganic polymers.

The formation of pure inorganic materials by the sol-gel route requires heating: dense glasses can be prepared around T_g; ceramic

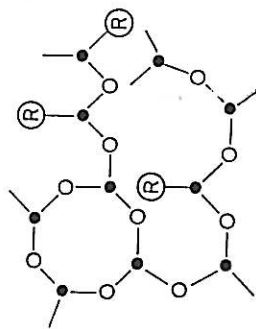


Figure 1a. Scheme of a glasslike structure, modified by organic groupings

● Si
○ O.

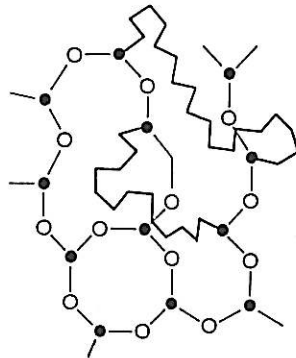


Figure 1b. Scheme of a glasslike structure, modified by additional, covalently bonded organic polymer chains.

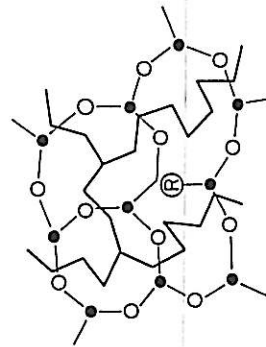
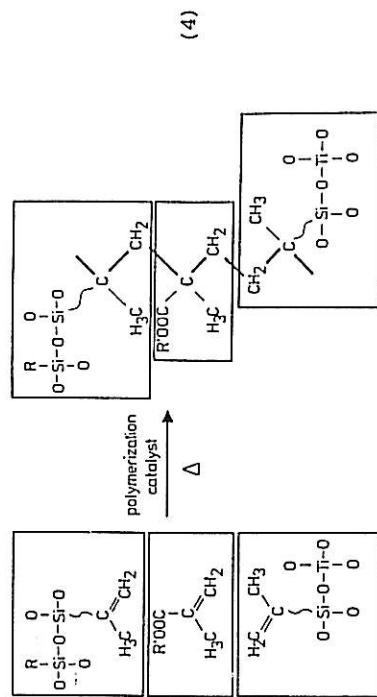


Figure 1c. Scheme of a glasslike structure, modified by an additional, polymeric network (interpenetrating).

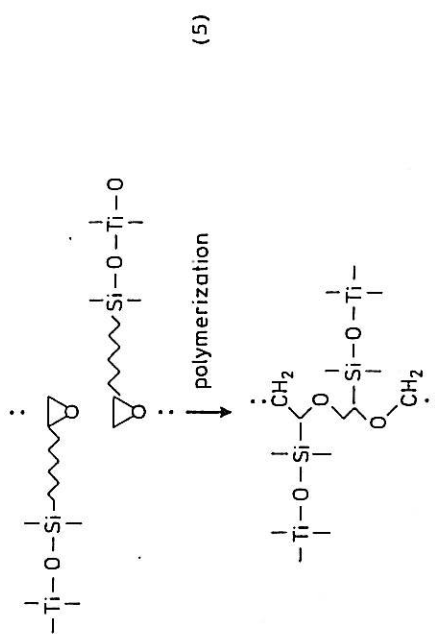


(4)

R = glycol group containing organic radical

R' = CH₃; C₂H₅OH

~ = -C₆H₄OOC-



(5)

Since sol-gel polycondensation and organic polymerization usually take place under different reaction conditions, the sequence of the reactions (organic polymerization prior to sol-gel condensation or vice versa) can be chosen by reaction conditions.

As an example, an adhesive material could be synthesized according to Equation 4 with an excellent adhesion to glass surface under wet conditions without the necessity to apply silane primers. The network of this adhesive has a glasslike structure and the adhesive power can be optimized by optimizing the content of ≡SiOR and ≡SiOH groups (34,30) (Figure 3).

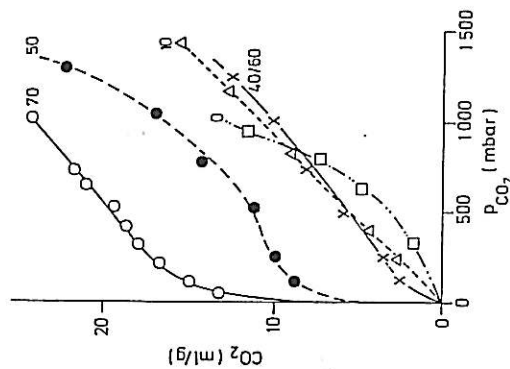


Figure 2. Adsorption isotherms of CO_2 on different network modified adsorbents: 70, network former SiO_2 to network modifier (am) ratio (molar): 30:70; 50, 50:50; 10, 90:10; 0, 100% SiO_2 ; 40/60, 40 SiO_2 and 60 $\text{CH}_3\text{SiO}_3/2$ (molar); specific surface areas all between 200 and 300 m^2/g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

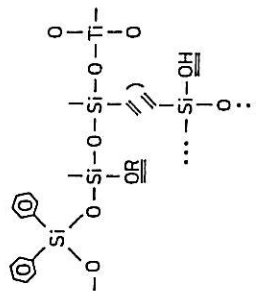
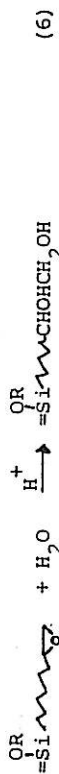


Figure 3. Reactive adhesive.

The adhesive was developed for application to seal food containers with alumina foils and to seal glass plates. In this case, the vinyl polymerization step can be carried out by UV light radiation through the already mounted glass plates with a photoactive radical initiator to cure the viscous adhesive material. Another application of this material is the development of diffusion barrier containing protective coatings on medieval stained glasses (31).

To introduce intrinsic hydrophilicity into silicone like structures (necessary to provide wetting within high oxygen diffusion materials for contact lenses), the ring opening reaction by H_2O addition was proved to be an adequate method (21) (Equation 6).



Since sol-gel condensation and ring opening reaction take place under the same reaction conditions ($\text{H}_2\text{O} + \text{H}^+$) and a reesterification reaction according to Equation 7 occurs,



a hydrolysis and condensation method was developed using an ester formation reaction as a water generation source, which leads to preferred condensation only. After reaching the desired degree of condensation, the addition of water enhances ring opening. This method (CCC = chemical controlled condensation) could be widely used in order to control different reaction rates of substituted and unsubstituted esters or different alkoxides (e.g. $\text{Si}(\text{OR})_4$ and $\text{Ti}(\text{OR})_4$). Very homogeneous materials could be synthesized with optical quality. Glycol group containing hydrophilic condensates, however, showed extremely poor mechanical properties. In order to improve the mechanical strength of this material, PMMA polymeric chains were synthesized with photoactivated radical initiators. The results are shown in Figure 4. The strengthening within this system is about a factor of five. This seems to be an extremely important finding with respect to the possibility of strengthening organic polymers by incorporating inorganic networks into organic polymers. The structure of the described contact lens polymer (21) is shown in Figure 5.

The polymerization reaction (Equation 5) leads to materials with extremely hard surfaces. Based on this, a new type of scratch resistant coating for different purposes could be developed. Table I gives some data of the high scratch resistant coating developed for CR 39 plastic eye glass lenses (39).

The data show the unique mechanical properties of this coating. The important item is that this coating can be applied at room temperature and cured at 90 °C and gives a clear film with optical quality. Typical properties of inorganic polymers (hardness) and organic polymers (coating as a lacquer and low temperature processing) could be combined in one and the same polymer.

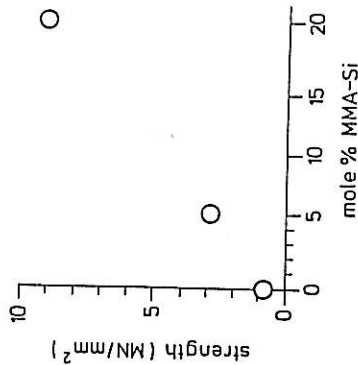


Figure 4. Increase of tensile strength by methacrylate addition to the polymer system $\text{TiO}_2/\text{SiO}_2/\text{SiO}_{3/2}\text{-R}$; $\text{R} = -(\text{CH}_3)_2\text{O-CH}_2\text{-CHOH-CH}_2\text{OH}$

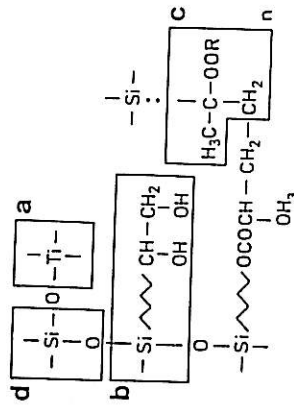


Figure 5. a, d: network formers
b: hydrophilic component
c: strengthening component

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Table I. Scratch and abrading tests of different coatings composition (mole-%): MeO_2 : 20; epoxysilane: 50; SiO_2 : 30

Test	Coatings and Polymers					
	CR 39 (uncoated)	PMMA (uncoated)	Coating 1	2	3	
A (load in g)	1 - 2	< 1	10	20 - 30	50	
B (haze in %) (200 rev.)	12 - 13	> 20	-	1.5	-	
C (haze in %)	4	-	-	1.2	-	
	15	-	-	6	-	

- 1 Zr-containing)
- 2 Ti-containing) coatings
- 3 Al-containing) diamond powder boron carbide powder

- A vickers diamond scratch test: diamond load of the first visible scratch (by microscope)
 B taber abrader: haze after abrading
 C special abrasion test with abrasive powders: haze after abrading.

Another application led to sensitive layers for coatings: ormocers including organic network formers as well as network modifiers could be developed (35) with reactive groupings for SO_2 , NO , and CO to be used as sensitive layers for new sensors. The reaction of a sensitive ormocer layer with gas molecules leads to a change of electric properties of the material. This change can be either monitored by a capacitance device (Figure 6) or by a field effect transistor (Figure 7).

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 -O-Ti-O-Ti-O- containing interpenetrating network was synthesized by use of an 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). The mechanical strength of the polymer increases remarkably.

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.

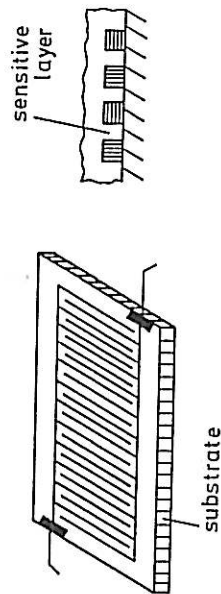


Figure 6. Scheme of a capacitance device sensor with an interdigitated structure.

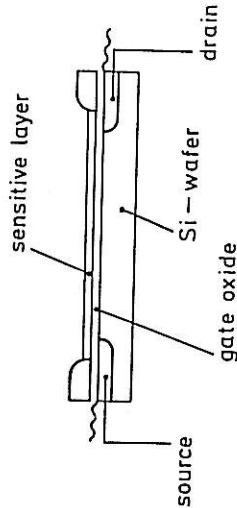


Figure 7. Scheme of a field effect transistor sensor.

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Acknowledgments

The author thanks his coworkers Dr. J. Strutz, Dr. B. Seiferling, and Dr. G. Philipp for supporting the experimental work and the Bundesminister für Forschung und Technologie of the Federal Republic of Germany and industrial companies for the financial support.

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