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MECHANICAL AND PHYSICAL PROPERTIES OF AMORPHOUS SOLIDS BASED ON $(CH_3)_2SiO$-SiO_2 GELS

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Résumé. - L'influence des conditions des réactions et des compositions sur les propriétés physiques des gels dans le système $(CH_3)_2SiO$-SiO_2 étaient etudiés. Ces matériaux sont préparés par une cohydrolyse et une cocondensation des composés $Si(OEt)_4$ et $(CH_3)_2Si(OEt)_2$. Ils étaient développés comme abrasifs à la durée d'application limitée et ils sont utilisés pour leurs effets cosmétiques et médicales, par exemple, pour amollir la peau humaine. Les réactions d'hydrolyse et de la condensation sont examinées par des méthodes infrarouges et par la spectrométrie de masse. Les matériaux étaient caracterisés par les techniques SEM, SAXS et BET. Pour définir les propriétés abrasifs on a développé une méthode spéciale.

Abstract. - The influences of reaction conditions and compositions on the physical properties of gels in the system $(CH_3)_2SiO$-SiO_2 were investigated. These materials are prepared by cohydrolysis and cocondensation of $(CH_3)_2Si(OEt)_4$ and were developed for being used as abrasive powders with limited effectiveness. They are applied for cosmetical or medical purposes, e.g. smoothening the human skin. Hydrolysis and condensation are monitored by IR, NIR and MS methods, for characterization of the materials SEM, SAXS, BET surface measurements, and a special abrasive test were used.

1. Introduction

Abrasives are widely used in technique and industry. In general abrasive powders have to be very hard in order to keep up their abrasion properties as long as possible. For special applications like cosmetic treatment or therapies of the human skin it is necessary to use softer abrasives or abrasives with limited effectiveness in order to avoid hurt. Moreover, these materials have to be absolutely free from toxic or irritating components.

For the latter reason, silica or silicones are very suitable, but silicones as abrasives are too soft, while silicas for skin therapy in general are too hard. The development of mixed polymers based on $[SiO_4]^{4-}$ and $[(CH_3)_2SiO_2]^{2-}$ should lead to materials, however, with suitable properties. Therefore, it seems to be necessary to know the basic influences of reaction conditions and compositions on the material properties. The reaction rates of hydrolysis, especially in mixed systems are of special interest, since reactive monomers are produced and the following cross-linking reaction will be strongly influenced by the concentration of these reactive monomers. The hydrolysis and condensation reaction will be affected by the type of catalyst, solvent, concentration of starting components and temperature.

2. Experimental

The materials were prepared by hydrolysis and condensation of $Si(OEt)_4$ and $(CH_3)_2Si(OEt)_2$ in ethanolic solution at room temperature in beakers or in a closed system under reflux conditions [1,2]. Aqueous solutions of HCl and ammonia were used as catalysts. The hydrolysis and condensation reactions were investigated by IR spectroscopy monitoring the H_2O deformation band at 1650 cm^{-1} [3,4]. Measuring the bands at 5155 (H_2O) and 4820 cm^{-1} (EtOH) in the NIR region it was possible to separate the hydrolysis from the condensation reaction. The viscosity of the reacting system was measured by use of an Ubbelohde viscosimeter. MS investigations were carried out

using a GC-MS system. For characterizing the abrasion behaviour of the materials the fraction between 0.3 and 0.4 mm was grinded between rubber plates under pressure simulating the abrasive procedure on the human skin and the amount of the uncrushed particles was determined. The specific surface area was measured by the BET method, microstructure was characterized by SEM and SAXS. The porosity was determined by an alcohol penetration method.

3. Results and discussion

In order to determine the influence of catalyst type and composition on the material properties, different series of materials were prepared. Solvent type and compound concentration and temperature (room temperature) were kept constant. To characterize the products, loose weight, porosity, BET surface, and the abrasion behaviour were determined. Table 1 gives a survey over the results obtained.

Table 1. Composition and properties of mixed condensates

Catalyst	composition SiO_2:$(CH_3)_2SiO$ (mol-%)	loose weight (g/cm^3)	BET surface (m^2/g)	porosity (ml/g)	abrasion test uncrushed fraction (wt.%)
1 N HCl	100: 0	0.97 (fraction 0.3-0.4 mm)	509	0.48	89
	90:10	0.83	707	0.71	94
	70:30	0.63	717	1.16	81
	50:50	0.50	439	1.30	90
3 N NH_3	100: 0	0.82 (as obtained (<0.3 mm))	91	not determined	very soft
	90:10	0.50	169		
	70:30	0.34	118		
	50:50	0.23	95		

Basic differences in the material properties are obvious. The specific surface areas are remarkably lower with the products prepared with ammonia as catalyst. The HCl catalyzed materials are compact, clear and homogeneous looking, the NH_3 catalyzed ones are cloudy and disaggregated. Similar results are reported by Brinker [5] on pure silicas. By SEM the typical differences in the microstructure become visible (fig.1).

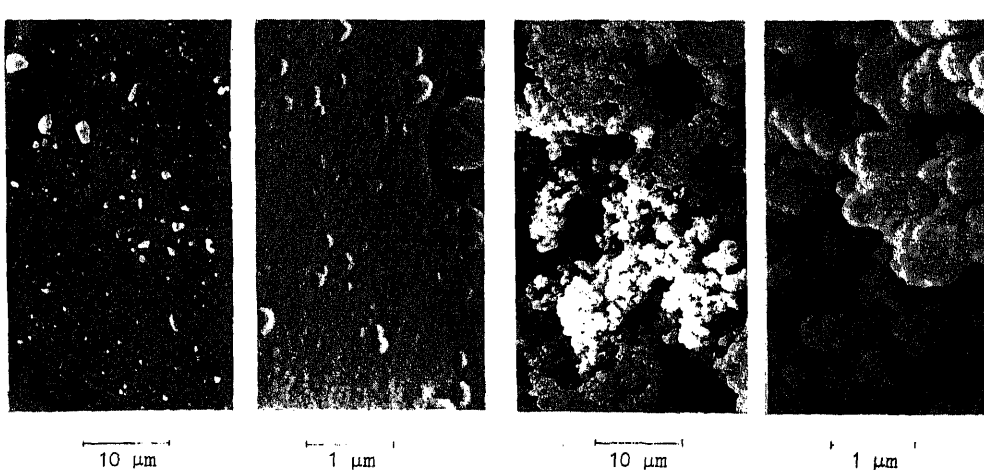

Fig. 1: Scanning electron micrographs of $SiO_2/(CH_3)_2SiO$ gels (molar ration = 70/30) prepared with 1 N HCl (left) and 3 N NH_3 (right) as catalysts.

SAXS measurements on HCl catalyzed samples show no structural inhomogeneity in the range of 10 to 100 nm despite of remarkable porosities and high BET surface areas. This might be due to the microporosity with pore diameters below 5 nm, as indicated by evaluation of BET isotherms. In the case of ammonia catalysis SAXS measurements show strong inhomogeneities. These inhomogeneities are observed with the rather disaggregated materials shown in fig.1 as well as with clear and compact materials which can be prepared with low NH_3 concentrations. The latter materials also show high specific surface areas and a clear and homogeneous appearance. So the SAXS plots have to be interpreted as structural inhomogeneities.

As a consequence, the differences in microstructure affect strongly the mechanical properties as indicated in table 1. How can these data be understood? As mentioned above, the process of hydrolysis and condensation should influence the cross-linking reaction and the mechanical and physical properties. With H^+ catalysis the rate of hydrolysis of $Si(OEt)_4$ is about $2\text{-}3\cdot10^3$ times slower than that of $(CH_3)_2Si(OEt)_2$ with a linear dependence of rate on H^+ concentration. The data could be confirmed by GC-MS investigation and by viscosity measurements of reacting systems of the single components. NH_3 kinetics are completely different, the hydrolysis rate of $(CH_3)_2Si(OEt)_2$ is slower than that of $Si(OEt)_4$ and decreases with increasing NH_3 concentration. Fig.2 shows schematically the chronological order of the different single reaction steps with HCl and NH_3 catalysis.

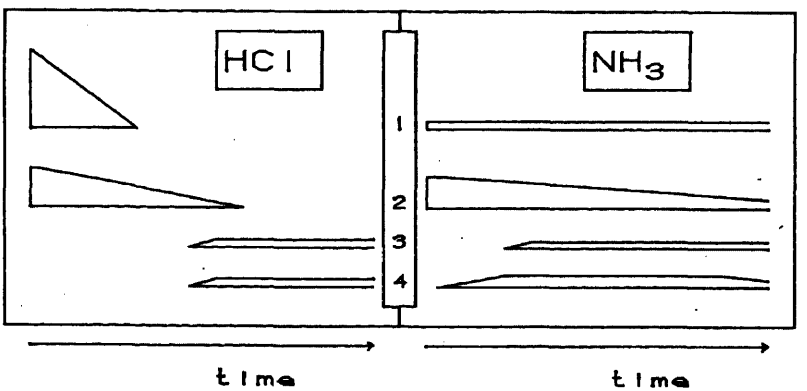

Fig. 2: Scheme of the chronological order of the single reaction steps of gel formation with HCl and NH_3 catalysis. The ordinate expansion of the bars refers to the reaction rate.

1: Hydrolysis of $(CH_3)_2Si(OEt)_2$
2: Hydrolysis of $Si(OEt)_4$
3: Condensation of $(CH_3)_2Si(OH)_2$
4: Condensation of $Si(OH)_4$

In the HCl catalyzed case a low ratio of condensation to hydrolysis rate results. Since condensation occurs slowly and high concentrations of reactive compounds of both types are available, a fairly homogeneous network may be built up. In the NH_3 catalyzed case, hydrolysis of $(CH_3)_2Si(OEt)_2$ takes place very slowly so that at first the condensation of $Si(OH)_4$ by forming SiO_2-rich primary particles may occur. Later on $(CH_3)_2SiO$ will be incorporated in increasing amounts. It is not quite clear up to now how far possible inhomogeneities resulting from these kinetic reasons may be related to the SAXS data. So far, more data have to be obtained.

Concerning the abrasion, only a weak influence of the composition could be observed (see table 1). While the compositions 100/0 and 90/10 are too hard, the composition 50/50 was too elastic due to the high amount of linear polymerizing $(CH_3)_2Si(OEt)_2$. Since a retaining of 60-80% of uncrushed particles after having performed the abrasion test was found to be most suitable for practical purposes, further optimization was based on 70/30 composition. By variation of the catalyst

concentration the abrasion could be varied in a wide range as shown in table 2.

Table 2. Abrasion behaviour of 70/30 condensates prepared with various catalyst concentrations

HCl concentration (N)	0.01	0.1	1	6	12
Uncrushed fraction (wt.%)	95	84	81	79	66
Loose weight (g/cm^3)	0.76	0.77	0.63	0.56	0.54

Catalyst concentrations between 6 and 12 N HCl lead to suitable products. The loose weight reflecting the disaggregation state of the microstructure checks well with the abrasion.

On the basis of these results a large scale preparation technique was developed. Since for technical purposes the reaction at room temperature requires too long time, the process was carried out under reflux conditions. Suitable products could be achieved by optimizing the catalyst concentration. By this, it was possible to prepare taylormade abrasives for very special purposes.

4. References

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