

HYBRID INORGANIC/ORGANIC POLYMERS WITH NANOSCALE BUILDING BLOCKS: PRECURSORS, PROCESSING, PROPERTIES AND APPLICATIONS

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Abstract. Hybrid polymers (ORMOCER[®]s, Ceramers) are composites with inorganic and organic nanobuilding blocks linked via stable covalent bonds based on organically modified silicon alkoxides and/or functionalized organic oligomers/polymers.

A method often used is the formation of the inorganic network by polycondensation reactions (e.g. Si-O-Si bond formation) in a first step, followed by the organic crosslinking (thermal curing at 80-180 °C or UV-processing). Another type uses the silylation of organic polymers, with subsequent hydrolysis and polycondensation reactions of the silanized units.

The paper focuses on the selection of precursors for various applications and the chemistry involved in processing. Basic properties and the application potential of ORMOCER[®]s as coatings, fibers and composites are presented. Property/composition relationships are shown for mechanical and permeation/barrier properties.

1. INTRODUCTION

Combining inorganic and organic structures on a molecular scale to form composites of polymer or glasslike materials is a challenging task due to very different formation reactions of inorganic and organic networks. So for example the classical glass and ceramic processing at high temperatures does not allow to incorporate organic structures due to their limited thermal stability. However by using soft chemical processes in solution this was made possible in the last 20-30 years and a huge variety of hybrid material compositions have emerged in the mean time [1-8]. According to Allcock [1] for polymers basically two types of hybrids can be distinguished:

Inorganic-organic polymers (IOP). They have inorganic elements in the main chain/network (example inorganic glasses) and may also have organic side groups. When the organic groups are reactive, additional organic crosslinking/polymerization is possible. If classical sol-gel processing [9]

of modified metal alkoxides is followed by organic polymerization or crosslinking the resulting hybrid materials are called ORMOCER[®]s.

Organic-inorganic polymers (OIP). These materials have C-atoms in the main chain/network and may contain inorganic elements in side groups connected to the organic network. Here also additional inorganic crosslinking is possible. Examples for these polymers are based f.e. on silylated organic oligomers/polymers with subsequent hydrolysis and polycondensation, and called Ceramers [5,10]. Ceramers are prepared by sol-gel processing of silylated oligomers/polymers, the organic network is previously formed in the precursor molecule.

Both IOP and OIP are examples of hybrid polymers. The idea of both of these concepts is to obtain a synergistic effect between inorganic and organic phases, not achievable otherwise by physical mixing of macroscopic phases as is usually made in classical composites. Since the structural units used for the controlled formation of hybrid polymers

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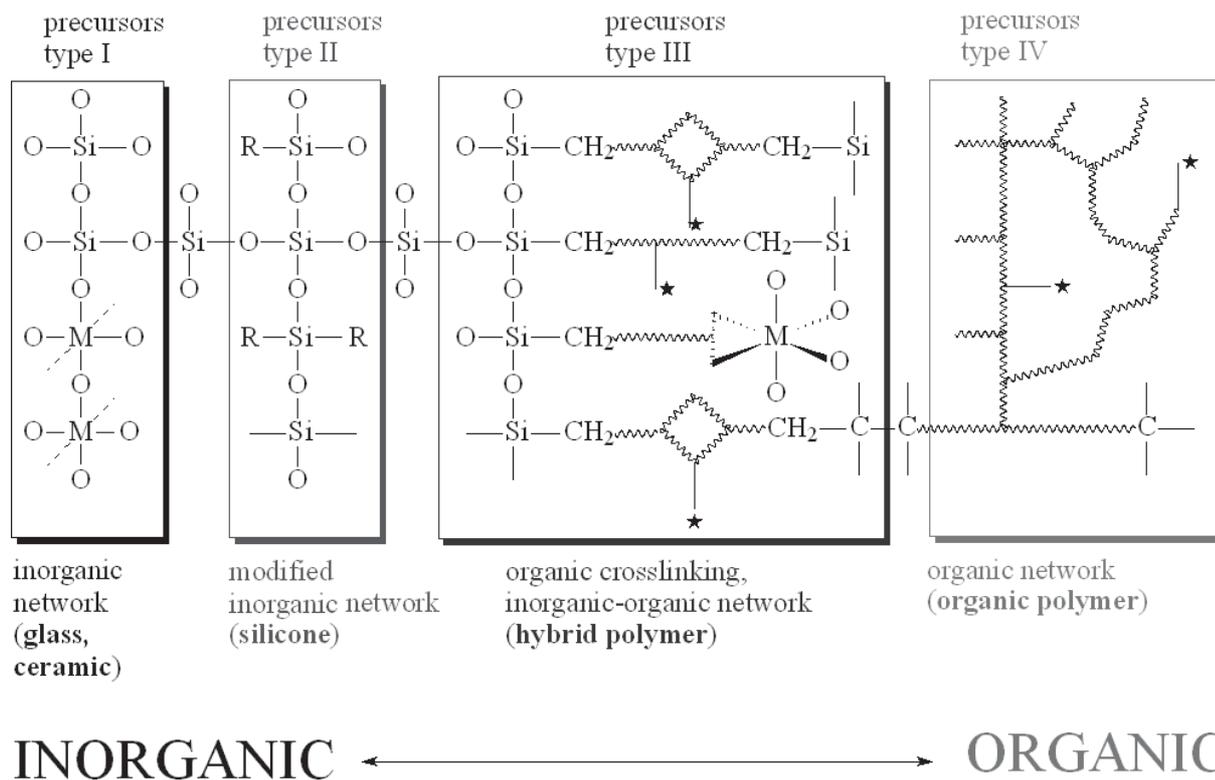


Fig. 1. Structural units of hybrid inorganic-organic polymers (ORMOCER[®]s, Ceramers) and precursor types used for preparation (*: additional functional groups).

are in the range of some nm up to maybe 10 nm [11, 12] they can be called nanoscaled or even molecular composites. There are other types of hybrid polymers with weak bonds (van-de-Waals, hydrogen bonds) between inorganic and organic phases, which are described in [2].

The focus of this paper are hybrid polymers having strong covalent bonds based on organically modified heteropolysiloxanes with some examples for OIP based on silylated organic polymers.

2. STRUCTURAL UNITS, PRECURSORS, PROCESSING

Hybrid polymers can be composed of structural units which span the whole range of more inorganic glass like up to compositions with a high content of organic networks similar to carbon based polymers as can be seen in Fig. 1. All structural units are connected via strong covalent bonds. The building principle of these hybrid polymers is based on different types of precursor molecules. These precur-

sors can be classified by their network forming or modifying roles [7]. Various polymerization, polycondensation or crosslinking reactions are possible. Basically four different types of precursors can be used for the synthesis of hybrid polymers:

type 1: inorganic network formers, alkoxides of Si (Tetramethoxysilane TMOS, Tetraethoxysilane TEOS), Al (Al-tri-sec-butylate), Ti (Ti-isopropylate), Zr (Zr-butylate), *etc.*

type 2: inorganic network formers with organic non-reactive modification. Due to the hydrolytic stability of the Si-C bond a wide variety of organic groups are available for the modification of the inorganic networks.

type 3: forming inorganic networks with reactive organic modification for crosslinking/ polymerization reactions or organic monomers/polymers with silylated end groups for crosslinking/ cocondensation via inorganic Si-O-Si bonds. These precursors are key elements for hybrid polymers.

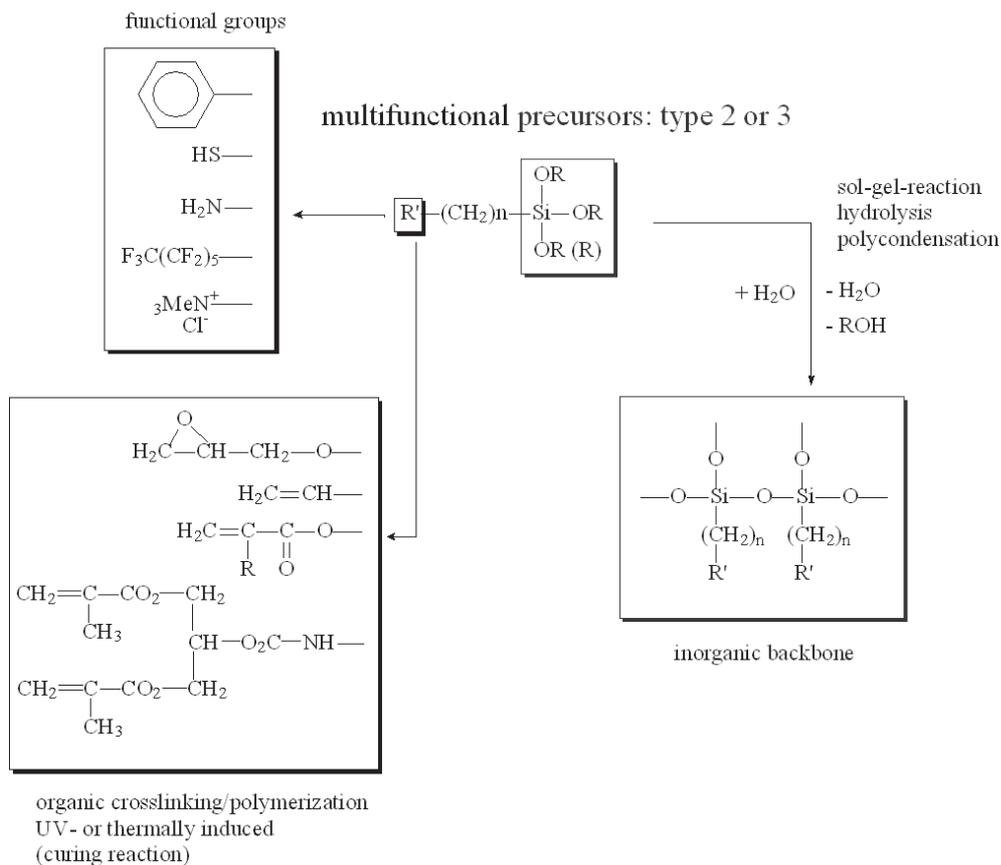


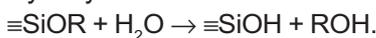
Fig. 2. Multifunctional precursors (type 2 or 3) for ORMOCER[®] synthesis.

type 4: organic monomers which can react via chemical crosslinking or polymerization reactions with the modified metal alkoxides.

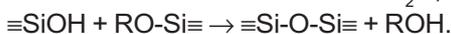
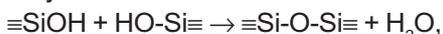
Fig. 2 shows examples for type 2 and 3 precursors. These precursors are multifunctional molecules in more than one sense. They have more than one reactive site and they have more than one type of reactive site (inorganic and organic).

The formation of the inorganic silica type or more general metal oxide network follows the classical sol-gel-route [9]. The reaction steps in case of Si alkoxides $\text{Si}(\text{OR})_4$ (R: Methyl, Ethyl, Propyl) are as follows:

Hydrolysis:



Polycondensation



Condensation with other metal alkoxides (Ti, Al, Zr) is possible at this stage. Due to varying reaction

rates of hydrolysis and polycondensation of different alkoxides care has to be taken that true cocondensation takes place leading to homogeneous materials. For the synthesis of ORMOCER[®]s this is the first processing step followed by organic crosslinking or polymerization. The thermal crosslinking of the organic groups is done at temperatures between 80 and 180° C or via UV-induced reactions. If OH-functionalized polymers like vinylalcohol/styrene-copolymers (molecular weight around 1200 g/Mol) or polyvinylbutyral – PVB (molecular weight 60000 g/Mol) are used around 10-20% of all available OH-groups are silylated (f.e. by the reaction of isocyanatosilane with the OH-functions) prior to the sol-gel reaction step. In this case mainly water based dispersions of the hybrid polymers can be achieved, which are self-curing systems without the need for additional thermal energy. By cocondensation with acrylate group containing silanes UV-curable systems can also be synthesized. The remaining OH-groups of the hybrid polymer play an important role due to their polar nature

in order to generate stable water based systems. These systems can be used as specially pigmented coatings for facades [13]. Other interesting compositions can be synthesized using silylated polyaniline in order to incorporate electronic conductivity into the composite [14].

3. PROPERTIES AND THEIR CONTROL BY BASIC COMPOSITION

In general the hybrid polymers which are based on precursors shown in Fig. 2 are nanoscaled materials with structural units smaller than 10 nm as indicated by SAXS measurements [11]. There are no crystalline or partly crystalline phases present and the polymers show high optical transparency and no absorption. ORMOCER[®]s are in general thermoset materials which are highly crosslinked and therefore stable towards chemicals and solvents.

Table 1 shows properties of hybrid polymers based on modified silica networks. As can be seen the properties cover a wide range of values, resulting from different types/amounts of precursors and the structural units connected with them. For example hybrid polymers can be highly insulating dielectric materials and by organic modification of the inorganic network, antistatic behavior, ion conductivity or even weak electronic conductivity can be achieved.

One of the main influence on the hybrid polymer properties is the amount and type of inorganic network. Some examples are shown below.

Mechanical properties: Comparing the stiffness of typical organic carbon based polymers (up to around 5 GPa) with inorganic oxidic glasses (Silica: 70 GPa) shows that the combination of organic and inorganic should give materials with high stiffness at high amounts of inorganic network formers. This was demonstrated in many cases [5, 15, 16]. The nature of the inorganic oxidic network also plays a major role. As was shown elsewhere, especially Al-O-Al containing epoxysilane based compositions have extremely good mechanical abrasion resistance [6]. However there are some general problems with high inorganic contents: The materials tend to become more brittle and the transparency is often lost. Another aspect is the prolonged processing time at higher temperatures in order to consolidate the inorganic network. So most of the systems used f.e. as abrasion resistant coatings have less than 50 weight % inorganic oxidic contents.

Table 1. Selected property range of IOP based on modified silica networks.

<i>property</i>	<i>values /unit</i>	<i>comment</i>
density	1,1–1,6 g/cm ³	without fillers
thermal expansion coefficient	50–200 ppm K ⁻¹ 18–70 ppm K ⁻¹	without fillers with fillers
thermal stability	from 180 up to 400 °C	< 5% weight loss (TGA)
Young's-modulus	from 0,013 up to 18,6 GPa	high organic/ polymer content high inorganic content
refractive index (optical wavelengths)	from 1,42 up to 1,65	very low values with fluorosilanes Ti-/Zr-oxidic networks, aryl modification
optical loss	≥ 0,3 dB/cm (1310,1550 nm) ≥ 0,06 dB/cm (633 nm)	without fluorination
specific electrical resistivity	10 ¹⁶ Ω cm 10 ⁸ Ω 10 ³ Ω cm 10 ² Ω	passivation antistatic H ⁺ /Li ⁺ -conducting solid electrolytes polyaniline based composites
dielectric number	≥ 3,2 at 10 kHz	coatings
dielectric loss	≥ 4x10 ⁻³ at 1 MHz	
dielectric strength	100 - 400 V/μm	coatings
oxygen permeability	as low as 10 cm ³ /m ² d bar up to 130000 cm ³ /m ² d bar	barrier coatings contact lenses, nonporous membranes

Permeation properties: Inorganic glasses have extremely low permeation rates for gases and water vapor, organic polymers on the other side have flexible, more open type networks and therefore suffer from high gas permeation when used in sensitive

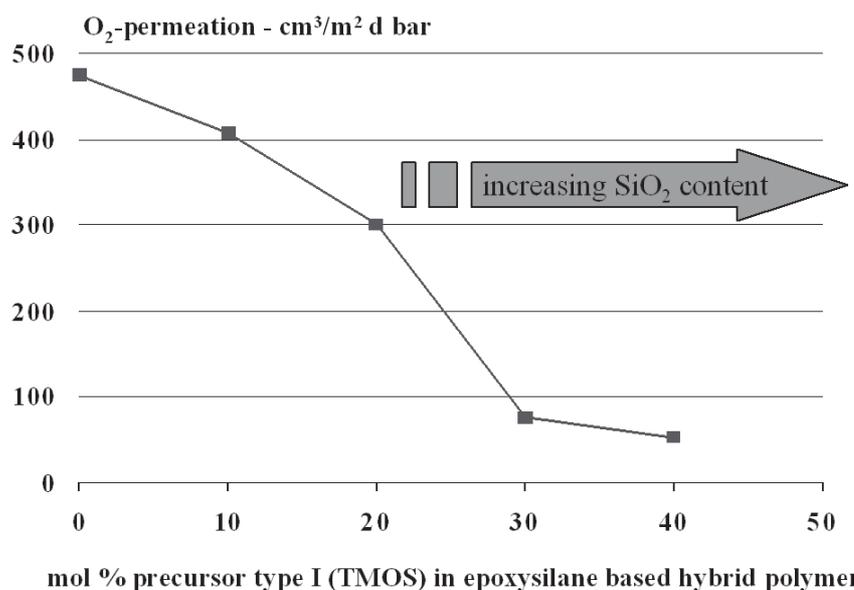


Fig. 3. Influence of Si-O-Si content (indicated by the molar amount of Tetramethoxysilane) on oxygen permeation rate of epoxysilane based IOP thin films on polypropylene foil.

applications. Fig. 3 shows the influence of the amount of inorganic network former of type I on the oxygen permeability. The permeation for oxygen drastically drops if the inorganic content is increased [11, 17]. If high permeation is needed hybrid polymers can also be useful if they contain high amounts of silicone type structures and more open organic networks [18].

4. APPLICATIONS

The sol-gel process is a very versatile method to generate various forms due to the intermediate sol-state: Coatings, particles and fibres. The generation of bulk materials in case of pure inorganic sol-gel compositions however is limited due to high shrinkage during the consolidation of the inorganic network [9]. In case of hybrid polymers due to the organic network and the reaction temperatures below 200 °C bulk compositions are much easier accessible.

The applications of ORMOCER[®]s are very widespread [12]. Especially functionalized coating materials (film thickness 1-10 μm) were very successfully developed within the last 15 years. Starting with transparent hardcoats for optical polymers [19, 20], dish-washer stable decorative coatings on crystal glasses [21] and transparent films with high barrier properties for polymer foils [17] various applications have found their way to industrial applications.

Another very successful material development based on ORMOCER[®]s was in the field of dental materials. Two families of dental composites are marketed worldwide, which are based on specially designed multi-acrylate-silanes [7, 22, 23]. Here the ORMOCER[®] is the hybrid matrix which is used together with inorganic fillers in order to prepare dental fillings with very low shrinkage during light induced curing, combined with excellent mechanical abrasion resistance and biocompatibility. Based on multi-acrylate-silane compositions also hollow fiber membranes were demonstrated with very interesting permeation properties [24].

Upcoming industrial applications are in the field of microoptics and microelectronics [25]. Here the excellent optical transparency (even in the near infrared regime) in combination with low temperature processing and good thermal and mechanical stability is used to prepare optical waveguides [26]. First experiments were also conducted in order to generate photonic crystals by 2-photon-induced polymerization [27]. Due to their UV induced polymerisation step ORMOCER[®]s can be used like photoresists showing low dielectric losses which makes them good candidates for passivation, interlayer dielectrics and encapsulation [28]. The functionalization of ORMOCER[®]s towards ionic conductivity [29, 30] can lead to application in thin film polymer batteries or fuel cells.

The basic interest in hybrid polymers stems mainly from the fact that having materials which have similar properties like inorganic glasses or ceramics but can be functionalized and processed like organic carbon based polymers at the same time is like having the best of both worlds.

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