Hybrid Nanocomposites for Nanotechnology
Lhadi Merhari
Editor

Hybrid Nanocomposites for Nanotechnology

Electronic, Optical, Magnetic and Biomedical Applications

Springer
To the Loving Memory of my late Mother Eleonora
Preface

With the advent of nanoscience and nanotechnology, the dream of scientists to engineer new functional materials combining the best specific properties of organic and inorganic materials is closer to reality. The traditional targeted application has been the reinforcement of plastics with the addition of inorganic fillers. Accelerated research over the past two decades, as evidenced by the large bulk of literature on mechanical properties of organic–inorganic composites, focused on systems such as clay/polymer nanocomposites, which are now exploited by the automotive industry worldwide. Although, in the low filler loading range, clay/polymer nanocomposites can replace traditional fiber-reinforced composites, there is still a long way to go before understanding the mechanisms of enhancement of major engineering properties of polymers and to tailor their nanostructure.

The driving force to edit the present comprehensive book has been to show that the applications of organic–inorganic nanocomposites extend far beyond the above-mentioned traditional mechanical applications and that hybrid nanocomposites should be considered as an attractive, versatile, technological platform for future electronic, optical, magnetic, and biomedical applications. Indeed, taking up challenges such as homogeneous dispersion of inorganic nanoobjects into a polymer matrix or tailoring of the multiscale nano-to-macro structure of the composites will contribute to the establishment of a solid unified hybrid nanocomposite technological platform for commercially-viable products revolutionizing various industrial sectors.

The generally-accepted definition of a hybrid nanocomposite is a material created by dispersing inorganic nanoparticulates into a macroscopic organic matrix. Since the discovery that the markedly enhanced electrical and thermal conductivity, optical and dielectric properties, and mechanical properties such as stiffness and strength of the resulting material are essentially because of the extraordinarily large interfacial “third” phase, hybrid nanocomposites constitute a fast-growing area of the field of nanotechnology. Nanoscience is now recognized as essential to understanding and predicting the correlation between nanocomposites’ enhanced properties and high surface-to-bulk ratio of the constituting inorganic nanocomponent, and to direct the synthesis strategy for on-demand functional hybrid nanocomposites. Clearly, cost-effective strategies ensuring high-precision spatial and orientational
control of the hierarchical structure will broaden the spectrum of hybrid nanocomposite applications from commodity plastic applications to high-added-value components in active devices such as photovoltaic cells, biosensors, light emitting devices, and energy storage systems.

It is the hope of the editor that Hybrid Nanocomposites for Nanotechnology: Electronic, Optical, Magnetic and Biomedical Applications will become an invaluable reference book introducing the reader to this fascinating field and will stimulate the creativity of academic, industrial, and governmental researchers active in materials science, chemistry, polymer science, surface science, semiconductor physics, electrical engineering, electronics, surface microscopy, spectroscopy, microelectronics, electrochemistry, photonics, data storage, sensors, energy storage, computational engineering, biology, microbiology, bioengineering, biotechnology, pharmacy, medicine, and oncology.

As the aim of this book is to address a large audience of readers, from Ph.D. students to senior researchers in the academic world and also from engineers to business people in various industrial sectors, it has been organized by practical applications rather than by scientific disciplines. This book consists of 17 chapters written by 37 international leading experts from 12 different countries: Australia, Czech Republic, Germany, India, Ireland, Italy, Japan, Korea, the Netherlands, Portugal, Spain, and the USA. It will provide a large coverage of applications in the industrial sectors where nanocomposites can bring a specific value and decisive competitive edge.

Each chapter is self-contained with cross references. For the unity of the book, an overlap in the chapters – namely nanocomposite synthesis methods specific to the targeted application – has been purposely kept to play the role of scientific thread. For the first time, this book will offer a complete perspective on the topic of hybrid nanocomposites and should serve as a comprehensive reference with its 2,500 bibliographic citations. The chapters presenting cutting-edge research are classified into four parts:

- Part I “Synthesis and Characterization of Organic–Inorganic Nanocomposites” contains five chapters on the recent developments in synthesis, processing, and characterization of various types of nanocomposites.
- Part II “Electronic and Magnetic Applications of Hybrid Nanocomposites” contains six chapters describing specifically designed nanocomposites for applications mainly related to the electronic and energy storage sectors. Promising applications of magnetic nanocomposites are also reviewed.
- Part III “Optical Applications of Hybrid Nanocomposites” contains three chapters focusing on innovative photonic devices.
- Part IV “Biomedical Applications of Hybrid Nanocomposites” contains three chapters with an emphasis on biosensors.

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This book is the result of the outstanding collaboration of all the distinguished authors who have dedicated their valuable time and effort to write state-of-the-art reviews. The editor is greatly indebted to all these leading experts for their commitment to excellence.

The editor wants also to express his deepest gratitude to Dr. Marie-Isabelle Baraton (University of Limoges, France), an internationally renowned expert in nanoscience and editor of leading books in the field, for her invaluable advice and critical review of the book.

Finally, special thanks are due to Ladislav Beránek, Christl Jeske, Helmut Lenhard, and Romana Leuschner for their kind support and encouragement.

Limoges, France

Lhadi Merhari
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Part I

Synthesis and Characterization
Chapter 1
Epoxy-Silica/Silsesquioxane Polymer Nanocomposites

Libor Matějka

Abstract Organic–inorganic (O–I) polymer nanocomposites are multicomponent and multiphase systems. Research of such complex systems is focused on understanding hybrid formation and on elaborating a general approach to control their structure, in order to synthesize a material with the required properties.

The present chapter deals with the O–I nanocomposites composed of an epoxy network as the organic matrix and silica or silsesquioxane (SSQO) domains as the inorganic “filler.” The inorganic phase is introduced in the organic matrix via two approaches: (a) in situ generation within the matrix by the sol–gel processing of alkoxy silane precursors, and (b) incorporation of well-defined nanobuilding blocks such as polyhedral oligomeric silsesquioxanes (POSS). Both molecular and phase structure evolutions were followed during the O–I network build-up. Relationships between hybrid formation, its structure and morphology, and properties were determined.

Hybrids with a wide range of structures and morphologies were synthesized, depending on the type and composition of the system and on the conditions of the polymerization procedure. Their morphologies ranged from that of an epoxy matrix with well-dispersed POSS units (at the molecular level), to that of the same matrix with inorganic clusters and aggregates of various sizes, to a bicontinuous O–I phase structure. Moreover, ordered (lamellar) structures were formed under suitable conditions. The mechanical properties of the O–I hybrids are described in terms of reinforcement of the organic matrix with an inorganic phase, which is dictated by the morphology of the system and the interphase interaction. The ways of controlling the interaction between phases are shown. The interpretation of the mechanical behavior of the O–I polymers is based on the structure-properties relationship and on the theoretical evaluation using composite models.
Abbreviations

Symbols
$\alpha$: Critical conversion, conversion at the point of gelation; $D_m$: Mass fractal dimension; $f$: Functionality of the reacting agent; $G_C$, $G_M$, $G_f$: Shear modulus of the composite, matrix and filler, respectively; $G'$: Equilibrium shear modulus in the rubbery state; $G'$, $G''$: Dynamic shear storage and loss modulus, respectively; $I$: Scattering intensity; $K$: Parameter characterizing strength of the interphase interaction; $M_c$: Molecular weight of the chain between junctions of the network; $q$: Scattering vector; $R_G$: Guinier radius; $r_{AE}$: Molar ratio of functional groups NH/epoxy; $r_{H_2O/Si}$: Molar ratio $H_2O/Si$; $T_g$: Glass transition temperature; $T_i$: Fraction of $T_i$ unit; $T_{5\%}$: Temperature, at which 5% loss of mass occurs by thermal degradation; $t_{gel}$: Time of gelation; $v$: Volume fraction; $v_E$: Crosslinking density of the network, (concentration of elastically active chains); $v_{AE}$: Volume fraction of free epoxide
chains; $\nu_{eb}$: Volume fraction of bound epoxide chains; $\nu_{Si}$: Volume fraction of the silica phase; $\nu_{ef}$: Effective volume of the filler; $\nu_f$: Volume fraction of the filler.

### 1.1 Introduction

High requirements on material properties result in the development of new types of multifunctional materials. A wide range of properties could be achieved in multicomponent polymer systems. These polymers form a complex structure and a multiphase morphology, which leads to a large variety of properties. Polymer nanomaterials have received a great deal of attention in basic and applied research in recent times.

Organic–inorganic (O–I) nanocomposite polymers, with an organic matrix filled with inorganic species of the size usually 1–100 nm, are a special category of nanomaterials [1–4]. Under convenient conditions, the O–I polymers show a synergetic effect of both phases, such as stiffness, thermal resistance, fireproof attributes in the inorganic phase, and toughness of the polymer. Generally, the O–I nanocomposites are synthesized by the top-down or bottom-up procedures. In the so-called top-down approach, the large micron-sized particles are disintegrated to form nanostructures. This method is typical of the nanocomposites prepared from layered silicates – clays.

The topic of this chapter is the preparation of the polymer nanocomposites by a bottom-up technique, i.e., by the build-up and growth of the inorganic nanostructures within a polymer matrix from a molecular level. The achievement of a fine dispersion of the nanofiller in a polymer matrix is a key problem of polymer nanocomposites. The small particle size and interparticle distances result in strong filler-filler interactions, and in a tendency to the formation of aggregates and agglomerates. Their presence could deteriorate the material properties. Therefore, the O–I polymers with in situ generated nanostructures are the prospective kinds of nanocomposites, because the initially reacting species are molecularly dispersed in a polymer. The integration of compatible organic and inorganic components at a molecular scale is achieved by the conventional sol–gel process chemistry [5, 6]. A variety of polymer systems – elastomers, thermoplastics, linear or crosslinked polymers – were filled with inorganic fillers formed in situ [7–10]. There are several methods of synthesis of the O–I polymer nanocomposites by this technique: (a) sol–gel polymerization of alkoxysilanes in the organic polymer matrix [1, 11–14], which is the most common procedure, (b) polymerization of organic monomers in silica gel pores or impregnation of the gel with an organic polymer [136], (c) simultaneous polymerization of organic and alkoxysilane monomers [137], (d) polymerization of reactants involving two types of functionalities as O–I precursors for formation of both organic and inorganic structures [15, 138].

The dimensions of an inorganic nanofiller are comparable with the size of a polymer, and therefore the nanocomposite behavior differs qualitatively from the classical microcomposites. The immense interfacial area is a typical feature of the
nanocomposites. Their exceptional properties are determined mainly by the interaction of the nanoparticles with the polymer at a molecular level, and by restriction of molecular dynamics at the interface. The interface interaction polymer-filler, immobilization of the polymer, interaction filler-filler, and nanostructure percolation in the polymer matrix play a crucial role. The improvement of mechanical properties (both stiffness and toughness) was observed when the interparticle distance was smaller than the particle diameter. In this case, the interphase can percolate through the system and dominate the properties [16]. To understand the behavior of the O–I nanocomposites, it is obvious that the perfect characterization of the nanocomposite structure at various length scales is necessary. This involves the geometry of the nanostructures, space and topological arrangement in the matrix, including the filler-filler and filler-polymer interactions.

The well-characterized nanocomposite systems are represented by the O–I polymers prepared from preformed nanoobjects, i.e., defined molecular nanobuilding blocks (NBB) [3, 17]. Various species have been used to serve as NBB, such as organically modified oligosilsesquioxanes, metal oxo-clusters, functionalized nanoparticles (metals, metal oxides), among others. Their synthesis was reviewed by Sanchez et al. [18]. The most promising NBB are functionalized metal oxo-clusters. Mainly, silicon-based NBB polyhedral oligomeric silsesquioxanes (POSS) exhibiting cage structures are of high importance.

This chapter will present the O–I polymer nanocomposites based on the epoxy systems with inorganic silicon-based structures generated by the sol–gel process in situ in the polymer matrix, or incorporated in the epoxy network as the well-defined nanobuilding blocks POSS. The evolution of the molecular and phase structure during formation of the epoxy-inorganic network, as well as morphology and thermomechanical properties of the nanocomposites, will be discussed. The effect of the main factors governing the structure of the nanocomposites, including the interface interaction, will be presented. The aim of the chapter is to describe the relationships between formation of the O–I polymer nanocomposite, its structure, and the properties that make it possible to control the structure and morphology and predict the properties.

1.2 Epoxy-Silica/Silsesquioxane Networks

Epoxy networks, as the most widespread thermosets, are often used as a polymer matrix of the O–I nanocomposites. Mainly diglycidyl ether of Bisphenol A (DGEBA) epoxy resin or, to a lesser extent, tetruglycidyl dianinodiphenylmethane (TGDDM) cured with aromatic diamines, such as dianinodiphenylmethane (DDM), dianinodiphenyl sulfone (DDS), or 4,4′-[1,3 phenylenebis(1-methylene)]bis(aniline) (BSA), are applied. However, epoxy matrices crosslinked with aliphatic amines, anhydrides, or dicyandiamide (among others) are also employed. Most often, high-$T_g$ epoxy networks are used for synthesis of nanocomposites; nevertheless, the rubbery epoxy matrices have also been reinforced [19].
Silicon-based inorganic nanofillers of a variable structure are applied for the epoxide nanocomposites. The silica nanoparticles [20, 21], layered clays [22, 23], or the silica and silsesquioxane (SSQO) structures generated in situ by the sol–gel process [24–28] are the most common nanofillers. Moreover, POSS containing epoxy networks have also been investigated [29–33].

In this chapter, special attention will be paid to DGEBA – poly(oxypropylene) diamine (Jeffamine, Huntsman Int.) networks – and mainly to the rubbery network DGEBA-Jeffamine D2000. Due to low glass transition temperature, the DGEBA-D2000 network is very sensitive to mechanical reinforcement with inorganic nanodomains, in contrast to the glassy epoxide networks.

The following epoxide-amine reactions take place during the network formation:

\[
\begin{align*}
R-\text{CH}_2-\text{CH}_2 + H_2N-R^1 & \rightarrow R-\text{CH}_2-\text{CH}_2-NH-R^1 & (1.1) \\
R-\text{CH}_2-\text{CH}_2 + R-\text{CH}_2-\text{CH}_2-NH-R^1 & \rightarrow R-\text{CH}_2-\text{CH}_2-N-C=O-R_1 & (1.2)
\end{align*}
\]

Composition of the epoxy-amine network is characterized by the molar ratio of functional groups \( r_{AE} (\text{NH/epoxy}) \). In most cases, the stoichiometric composition is employed, \( r_{AE} = 1 \).

Two ways of introducing the inorganic nanodomains in the network matrix will be discussed:

(a) In situ generation of inorganic nanodomains by the sol–gel process within the organic medium will be reported in the first part of the chapter (Sect. 1.3). This procedure enables the generation of various inorganic structures, including the bicontinuous O–I phase morphology. However, the precise control of the final morphology is difficult, and the structures are polydisperse in size and heterogeneous in the chemical composition.

(b) Incorporation of well-defined nanobuilding blocks – POSS – will be the topic of the second part (Sect. 1.4). The initial control of the particle size and volume fraction is the main advantage of this procedure. Formation of the nanocomposite morphology takes place by aggregation of the NBBs within the matrix.
The nanocomposites prepared by procedures (a) or (b) differ in the character of the inorganic nanodomains. While the sol–gel process generates chemical clusters with strong covalent structures, in the case of NBB the inorganic domains are formed by the physical aggregates of the nanosized units with weak physical intradomain interactions.

The phase or microphase separation of organic and inorganic structures is a typical feature occurring during the synthesis of the O–I networks. The interphase interaction is of primordial importance for the nanocomposite morphology. Physical interaction or even covalent bonding between O and I structures leads to an improvement of the system compatibility. In this case, homogeneous and transparent hybrid materials are produced. The common classification of O–I polymers [3] is based on the strength of the interphase interaction, and includes systems with no interactions or weak physical interactions and the polymers with strong covalent bonds between phases. Both types of epoxy-based O–I nanocomposites will be discussed – interpenetrating O–I networks without an intentional interphase bonding (Sect. 1.3.2) and the organic networks with defined grafting to the inorganic nanodomains (Sect. 1.3.3).

The organic matrix of the nanocomposites discussed in this chapter is formed by the epoxy network, with the exception of the alkoxysilane-endcapped oligomer (ASO) hybrid. This O–I network involves the urethane or urea groups, while no epoxide monomer contributes to the network build-up. However, by its characteristics (nature of the polymer network chains, SSQO nanodomains, topology of the O–I network), this hybrid closely corresponds to the discussed series of the epoxy-silica/SSQO networks, and hence it has been included in this chapter.

### 1.2.1 Experimental Techniques of Nanocomposite Characterization

A wide range of experimental techniques have been used to follow the process of formation of the hybrids and to characterize the structure, morphology, and properties of O–I nanocomposites.

#### 1.2.1.1 Formation of O–I Hybrids

The process of O–I hybrids formation includes reaction kinetics, evolution of both molecular and phase structures during polymerization, gelation of polyfunctional systems, increase in crosslinking density in the postgel stage, as well as a possible vitrification.

Differential scanning calorimetry (DSC) or the spectroscopic methods like Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) are typically used to follow the kinetics of the polymerization involving determination of conversion of functional groups. The evolution of the molecular structure during the polymerization is investigated in the pregel stage by using size exclusion chromatography (SEC) and
mass spectrometry (MALDI), while scattering techniques, chemorheology methods, or dielectric spectroscopy (DES) can be applied even in the postgel stage.

Chemorheology and dynamic mechanical analysis (DMA) are useful mainly for in situ study of network formation by polymerization of polyfunctional systems. Gelation is a crucial phenomenon in network build-up, and a simple way of in situ determination of the gel point is provided by chemorheology. The gel point is roughly characterized by a steep increase in the dynamic modulus $G'(t)$ during the reaction. A precise determination of the point of gelation is performed by using a power-law rheological behavior at the critical state [34]. The loss factor $\tan \delta (=G''/G')$ measured during the crosslinking is independent of measurement frequency at the gel point.

The O–I hybrids are heterogeneous systems, and a phase or microphase separation takes place during polymerization. Small-angle X-ray scattering (SAXS) or dynamic light scattering (DLS) are the techniques used to follow evolution of the phase structure in formation of the O–I networks.

### 1.2.1.2 Characterization of O–I Hybrids

O–I hybrids are multicomponent and multiphase complex systems. Therefore, the multiscale approach of characterization is applied to fully describe the structure, morphology, and properties of the O–I hybrids.

Local structure at the atomic scale is determined by NMR and FTIR. In the case of the epoxy-silica/SSQO nanocomposites, the $^{29}$Si NMR spectroscopy is a method to determine a local structure of the silica or SSQO domains. The NMR analysis provides fractions of the structural units $Q_i$, corresponding to Si atoms with $j$ hydrolyzed groups (Si–OH) and $i$ siloxane bridges (Si–O–Si). Distribution of these structure units characterizes the structure topology of silica. The condensation conversion is defined as $\alpha_{Si} = \Sigma iQ_i/4$. In the case of trialkoxysilanes, the formed SSQO structure is described by the distribution of $T_i$ units, i.e., the structural units with $i$ siloxane bonds –O–Si– attached to the central atom. The conversion is defined as $\alpha_{Si} = \Sigma iT_i/3$.

\[
\begin{align*}
\text{OH} & \quad \text{R-Si-OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{O-Si-} \\
\text{R-Si-O-Si} & \quad \text{OH} & \quad \text{R-Si-O-Si} & \quad \text{O-Si-} & \quad \text{O-Si-} \\
\text{O-Si-} & \quad \text{T}_0 & \quad \text{T}_1 & \quad \text{T}_2 & \quad \text{T}_3
\end{align*}
\]

Macromolecular scale structure is investigated by the scattering methods – SAXS, neutron scattering (SANS), or static and dynamic light scattering. In addition to the size of the polymers or heterogeneity domains, the scattering methods also give a geometrical description of the structures using the concept of fractal geometry.
[35], because random processes of polymerization or aggregation usually lead to the formation of fractal objects. The fractal structure is characterized by mass fractal dimension $D_m$, which is a measure of the compactness or the shape of the fractal object. $D_m$ describes volume distribution of a mass, $m$, as $m \sim r^{D_m}$, where $r$ is the radius of the fractal object. The relation $1 < D_m < 3$ holds for the mass fractals. The fractal dimension can be experimentally determined by the scattering methods, e.g., SAXS, from the slope $x$ of a linear part of the scattering curve in log-log graph, $I(q) = q^{-x}$. $I$ is the scattering intensity and $q=(4\pi/\lambda)\sin \theta$ is the magnitude of the scattering vector. The exponent $x$ corresponds to mass fractals with fractal dimension $D_m = x$. The size of heterogeneities can be estimated by using the expression $d = 2\pi q_{\min}$ ($q_{\min}$ is a minimum $q$ corresponding to the linear part of the scattering profile).

The larger length scale – supramolecular structure or morphology – is determined by electron microscopy – scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). These techniques, of course, provide information on smaller length scales as well. DMA and DES are powerful indirect techniques to investigate the phase structure. Wide-angle X-ray scattering (WAXS) and DSC are employed to determine crystallinity of the material.

The interphase (polymer-filler) interactions in composites are examined using various techniques. Mainly, the viscoelastic properties (temperature, strain, or frequency dependence) are the perfect tool to detect the interaction between phases by DMA. Determination of the chain immobilization evidenced by a new relaxation process occurring at a higher temperature is the simplest approach. Moreover, the nonlinear behavior of composites manifests itself by a decrease in modulus at a low strain amplitude – the so-called Payne effect [36] – and is assumed to reflect the dynamics of polymer at the interface [37, 38], thus characterizing the polymer-filler interaction. In addition, other relaxation methods like DES, thermally stimulated depolarization currents (TSDC), or the NMR relaxation techniques are applied to follow the polymer chain dynamics and to investigate the interaction. In addition, swelling experiments are used to evaluate the interaction by assuming that the swelling of the matrix is completely restricted at the particle surface, in accordance with the Kraus theory [39].

Mechanical properties are determined by DMA and stress-strain mechanical testing. Thermal properties such as glass transition temperature $T_g$, melting of crystalline domains, and thermal stability are determined by DSC, DMA, DES, or thermal gravimetry analysis (TGA).

1.3 Organic–Inorganic Networks with In Situ Generated Silica/SSQO Nanodomains

1.3.1 Sol–Gel Process

The sol–gel process includes a hydrolytic polycondensation of organometallic precursors such as silicates, titanates, and aluminales. The alkoxysilane compounds
R_{n}\_\_\_\_\_n-Si(OR')_n are mainly used as precursors of an inorganic phase formation. The sol–gel process (1.3–1.5) of alkoxysilanes results in the formation of linear polysiloxane (R_2SiO)_n or branched and crosslinked silsesquioxane (RSiO_{3/2})_n from trialkoxysilanes, as well as silica (SiO_2)_n structures from tetraalkoxysilanes. Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) are the most common precursors of the in situ formed silica phase.

\[
\begin{align*}
OCH_2CH_3 \\
CH_3CH_2O-Si-OCH_2CH_3 \\
OCH_2CH_3
\end{align*}
\]

TEOS

hydrolysis \quad Si(OEt)_4 + n H_2O \rightarrow Si(OEt)_{4-n}(OH)_n + n EtOH \quad (1.3)

condensation \quad Si-OH + HO-Si \rightarrow Si-O-Si + H_2O \quad (1.4)

Si-OH + RO-Si \rightarrow Si-O-Si + H_2O \quad (1.5)

\[
\begin{align*}
\text{silica network}
\end{align*}
\]

The sol–gel reactions make possible a relatively easy incorporation of a pure inorganic phase into an organic matrix. A low-temperature procedure, high purity of reactants, and the possibility of mixing of precursors of organic and inorganic phases at the molecular level are the main advantages of this technique. Alcohols (ethanol, isopropanol) or THF are usually used as solvents for the sol–gel reactions. Water content is characterized by the mole ratio \( r_{H} = H_2O/Si \). The stoichiometric water amount corresponds to the ratio \( r_{H} = 2 \) for tetraalkoxysilanes, and \( r_{H} = 1.5 \) for the trialkoxysilane monomers, taking into account both hydrolysis and condensation reactions.

The sol–gel process is acid- or base-catalyzed and the type of catalysis, water content, solvent, and temperature affect the reaction mechanism and the resulting structure of the silica phase [6, 40]. The kinetics of the process, including the simultaneous hydrolysis and condensation, were generally studied by Assink and Kay [41].

Two types of growth processes are proposed in the silicate systems: the reaction-limited cluster-cluster aggregation and the monomer-cluster aggregation [42]. The theory predicts the values of fractal dimension \( D_m = 2.1 \) for the reaction-limited
cluster-cluster reaction, and $D_m = 3.0$ for the monomer-cluster aggregation. Experimental SAXS results reveal [35] that mass fractals with $D_m \sim 2.1$ are formed during the sol–gel processes catalyzed with acid, which is consistent with the cluster-cluster reaction. In contrast, the monomer-cluster aggregation mechanism dominates in base catalysis, resulting in formation of more compact mass or surface fractals corresponding to colloidal particles with $D_m \leq 3.0$.

The effect of catalysis will be demonstrated by comparison of the action of the acidic, $p$-toluenesulfonic acid (TSA), basic benzyl dimethyl amine (BDMA), and pH neutral dibutyltin dilaurate (DBTDL) catalysts. Moreover, the typical epoxy hardeners, primary amines, show a catalytic effect for the sol–gel polymerization comparable to weak bases. The epoxy hardener Jeffamine D2000 has another special function in the hybrid system. In addition to being the crosslinker and catalyst, the poly(oxypropylene) chain of D2000 acts as a compatibilizer of the organic and formed silica phases.

1.3.1.1 Sol–Gel Polymerization of TEOS

The sol–gel polymerization of TEOS in isopropanol (IP) solution results in formation of silica gels. The catalysts govern the relative rates of hydrolysis and condensation, gelation of the system, and final morphology of the silica gels, including a possible phase separation. The rate of TEOS consumption, mainly due to hydrolysis, decreases in the series of catalysts with increasing basicity: TSA >> DBTDL > D2000 > BDMA >> no catalyst [43].

The acid catalysis by TSA promotes a fast hydrolysis; 50% of TEOS is reacted in 3 min at room temperature. As a result, a large fraction of the hydrolyzed products is formed. However, the condensation is slow, and only oligomer products are formed at room temperature during 24 h. Gelation of TEOS takes place at a reasonable time only on heating at a very high conversion (in 9 h at 80°C). The transparent gels are produced by using both TSA and DBTDL. The SAXS analysis reveals formation of small heterogeneities corresponding to the open mass fractals with fractal dimensions ($D_m$)$_{TSA} = 2.2$ and ($D_m$)$_{DBTDL} = 2.5$.

The reaction progress is different under nucleophilic catalysis with BDMA or D2000, and a more heterogeneous system is developed. The rate and extent of hydrolysis is lower compared to TSA catalysis, and less hydrolyzed products prevail. Half the TEOS is reacted in only 30 h at room temperature, using BDMA. In contrast, however, the condensation is effectively catalyzed, and high-molecular-weight products are formed from the very beginning of the reaction. Large compact silica structures of a high fractal dimension appear. The system phase-separates; precipitates or cloudy microgels emerge in the early stage and, in the case of BDMA, no macrogelation occurs. The morphology of the system prepared by using a higher concentration of D2000 becomes more homogeneous because of the solubilizing effect of poly(oxypropylene) chains on silica. Polymerization leads to an opalescent gel in a short time, at room temperature.
Structure evolution during TEOS polymerization includes formation of strongly cycled products – polyhedral cyclics [139, 140]. Due to the extensive cyclization, gelation is substantially delayed with respect to the theory, even under the relatively homogeneous conditions of acid catalysis. The classical theory of network formation predicts the critical conversion \( \alpha_c \) for a gel formation in polymerization of an \( f \)-functional monomer in the ideal case [44]:

\[
\alpha_c = \frac{1}{(f-1)}
\]  

For polymerization of a tetrafunctional monomer TEOS, the theoretical value is \( \alpha_c = 0.33 \), while the experimental critical conversion is \( (\alpha_c)_e = 0.83 \) (Ng et al. 1995).

### 1.3.2 Interpenetrating Epoxy-Silica Networks

Various kinds of hybrid epoxy-silica networks with in situ formed silica have been synthesized and investigated [19, 24, 25, 28, 45, 141]. Usually, the silica phase was produced within the network matrix by the hydrolytic polycondensation of TEOS. However, the nonaqueous synthesis of nanosilica in an epoxy matrix has also been reported [46].

#### 1.3.2.1 Network DGEBA-D2000-TEOS

We will describe the formation, structure, and properties of the epoxy-silica interpenetrating network (IPN) DGEBA-D2000-TEOS, consisting of the epoxide-amine network DGEBA-D2000 and the silica network in situ generated by the sol–gel process from TEOS [43, 47, 48]. Formation of the silica phase within the organic network depends on the method of preparation (see Scheme 1.1):

(a) The simultaneous polymerization of the organic monomers and TEOS,
(b) The sequential polymerization consisting in polymerization of TEOS within the preformed epoxide network.

**Scheme 1.1** Synthesis procedures of the O–I networks with in situ generated silica
Synthesis Procedures of the Hybrid Networks

*Simultaneous Polymerization*

The network synthesis has been performed by one- or two-step procedures.

*One-Step Polymerization*

The reaction mixture of the monomers (DGEBA, D2000, TEOS) and water was homogenized with the cosolvent isopropanol (IP), and both formation of the DGEBA-D2000 network and sol–gel polymerization of TEOS proceeded simultaneously. Hydrolysis and condensation of TEOS was performed at a molar ratio \( \text{TEOS}:H_2O = 1:3(\rho_H = 3) \) in IP solutions in the volume ratio TEOS:IP = 45:55. The reaction was catalyzed with TSA or DBTDL and the polymer base catalyst D2000. While 2 mol% TSA/TEOS was used for catalysis, the concentration of the catalytic NH\(_2\) groups in D2000 reaches 7–21 mol%/TEOS in different hybrid systems. Hence, an amine excess was applied in the hybrids. The synthesis temperature regime was as follows: \( T = 20^\circ\text{C} \) 2 h, \( 90^\circ\text{C} \) 2 days, \( 130^\circ\text{C} \) 2 days. The one-step polymerized epoxy-TEOS hybrid is indicated as ET-1.

*Two-Step Polymerization*

TEOS was prehydrolyzed under acid catalysis at room temperature, and then mixed with the organic components DGEBA-D2000 to start the “simultaneous” formation of both organic and inorganic phases. The hybrid is indicated as ET-2.

*Sequential Polymerization*

The epoxide network was prepared first by reaction of DGEBA with D2000 at \( 130^\circ\text{C} \). The cured network was swollen in the mixture TEOS-H\(_2\)O-IP at room temperature up to equilibrium. The swollen network was then heated in a closed vessel at \( 90^\circ\text{C} \) for 5 days to polymerize TEOS under TSA or DBTDL catalysis, and to develop the silica phase within the epoxide network. Final curing was performed in vacuum at \( 130^\circ\text{C} \) for 3 days. The content of silica in the network was controlled by composition of the swelling medium TEOS-IP. The hybrid is indicated as E1-T2.

Formation of the Epoxy-Silica Networks

*Simultaneous Polymerization*

During the simultaneous procedure of the hybrid IPN synthesis, the two independent reaction mechanisms are simultaneously operative, i.e., the reaction of the epoxy and amine monomers to form the DGEBA-D2000 polymer network, and the hydrolytic polycondensation of TEOS to form the silica phase. The structure evolution and final morphology of the epoxy-silica network is sensitive to the polymerization
procedure and mainly to catalytic conditions. The sol–gel process of TEOS in the DGEBA-D2000-TEOS hybrid system proceeds in the presence of both catalysts – TSA and D2000. In this case, the relative concentration of the catalysts is crucial for the sol–gel kinetics, silica structure, and morphology. Evolution of the silica structure by the sol–gel process is much faster under given experimental conditions than formation of the epoxide-amine network. While the silica system gels rapidly at room temperature, gelation of the stoichiometric epoxide network occurs only in 10 h at 80°C. Consequently, during the “simultaneous” polymerization, the silica network is formed first at room temperature, followed by a build-up of the epoxy-amine network at an increased temperature.

One-Step Polymerization

The sol–gel process in the one-step polymerization is base-catalyzed because of a molar excess of D2000 content over TSA concentration. The initially homogeneous mixture microphase-separates in the reaction, due to an early formation of high-molecular weight polysiloxane chains typical of base catalysis of TEOS polymerization. Evolution of the silica structures during polymerization is shown in Fig. 1.1a, depicting SAXS profiles of the reaction mixture at an increasing reaction time [47]. The scattered intensity of the SAXS profiles gradually increases during the reaction as the siloxane/silica structures grow. Gelation of the silica structure occurs in 81 min under given conditions at room temperature, according to independent chemorheology measurements.

The size of the forming siloxane polymers evaluated as the Guinier radius, \( R_G \), from SAXS analysis is concentration-dependent, and is larger in the diluted solutions, \( R_G \sim 15 \text{ nm} \). This fact implies that in the reaction mixture an overlap of the forming polysiloxane clusters occurs from the beginning of the reaction. The Guinier analysis provides a spatial correlation length, \( \xi \), within the overlapped polysiloxane clusters where intermolecular interferences contribute to the scattering profile. At the gel point, Guinier radius reaches the value of the spatial correlation length in the gel, \( \xi \sim 10 \text{ nm} \). A cluster overlap was also reported by Schaefer and Keefer [35] during the first step of the two-step acid-acid catalysis with sub-stoichiometric water content.

In the dilute system, the individual clusters are separated and their true size can be determined. SAXS intensity profiles of the reaction system after dilution, as shown in Fig. 1.1b, characterize the inner structure of the polysiloxane cluster. In contrast to the smooth scattering curves of the bulk reaction mixture, an increase in intensity at low \( q \) values as well as the break on the curve at \( q \sim 0.1 \, \text{Å}^{-1} \) appear in the diluted solutions. The shape of this profile is interpreted by formation of small domains with a diameter \( d \sim 3 \text{ nm} \) (according to the Guinier analysis) of a higher branching density within a large “heterogeneous” polysiloxane cluster (\( R_G \sim 15 \text{ nm} \)). These domains are formed by nonrandom branching under base catalysis. The inner siloxane groups in the chain \((-O-)_2 \text{Si(OC}_2\text{H}_5)_2=O\text{H}_n\) and the branched groups \((-O-)\), Si–OH are more reactive than the terminal ones \(-O\text{Si(OC}_2\text{H}_5)_3=O\text{H}_n\) [6], which results in formation of more branched and compact domains.
within the “heterogeneous” chain. On the contrary, under acid catalysis, the terminal groups react preferably and the chain grows at the end to form linear sequences. The size of the “branched” subunits in the base-catalyzed system increases during
the polymerization and their number grows, as revealed by the shift of the break to lower $q$ and by an increasing scattered intensity. The branched parts of the cluster become gradually interconnected, and finally fill in the whole cluster before the gel point and the break on the SAXS curve disappears. In bulk systems, the inner structure of the clusters is screened by their overlap, and hence no break on SAXS profiles corresponding to subunits is observed.

The forming structures show fractal behavior, as revealed from linearity of the intensity curves of the reaction mixture [35]. The change in the inner structure of the chain during the polymerization is shown by the gradual growth of the fractal dimension $D_m$ of the polysiloxanes in the reaction mixture, as illustrated in Fig. 1.2. The high fractal dimension reaching the value $D_m > 2.5$ after the gel point corresponds to a relatively compact structure. The large value of the fractal dimension can be explained by the participation of the reaction-limited monomer-cluster type reaction mechanism. This is the result of the presence of the monomer in the reaction mixture even at a late reaction stage, due to slow hydrolysis under base catalytic conditions.

Two-Step Polymerization

Two-step acid-base polymerization is an optimum method for a fast formation of the inorganic structure. The procedure consists of prehydrolysis of TEOS in an acid medium in the first stage, followed by the build-up of a network in the presence of nucleophilic D2000 in the second stage. The formation of silanol groups in the acid medium serves as an initiation step for the subsequent condensation under base catalysis. Gelation of TEOS at the D2000-catalyzed reaction is significantly accelerated by the acid prehydrolysis. The dependence of gelation time $t_{gel}$ on the time interval of the hydrolysis in the first step is shown in Fig. 1.3. Only 5 min of the

![Fig. 1.2 Increase in fractal dimension $D_m$ of the polysiloxane structures during the one-step polymerization of DGEBA-D2000-TEOS hybrid](image-url)
Acid prehydrolysis, corresponding to a conversion of more than 50% of TEOS, results in the dramatic acceleration of gelation in the second base-catalyzed step from ~100 to approximately 2 min. The prehydrolysis of TEOS also prevents precipitation of silica or microgel formation in the basic medium. The transparent gels are built-up under these conditions.

Evolution of the structure during the two-step polymerization of TEOS in the hybrid system DGEBA-D2000-TEOS significantly differs from that in the one-step process. In the first, acid-catalyzed step, a fast formation of the small particles with a size of ~2 nm takes place. The SAXS profiles in Fig. 1.4 illustrate the corresponding structure build-up at large scattering angles. These siloxane structures are low-molecular weight small cyclics formed by intramolecular condensation, in agreement with cage-like structures determined by Himmel et al. (1990) and Ng et al. (1995). Acid catalysis thus encourages not only fast hydrolysis but also condensation, to form small condensed structures in the early reaction stage.

The mixing of the prehydrolyzed TEOS with the system components DGEBA and D2000 results in a very fast polycondensation and gelation within 1–2 min. Figure 1.4 depicts an increase in the scattered intensity at low angles as the sizes of heterogeneities of the system grow. This second sol–gel step is catalyzed with 

**Fig. 1.3** Time of TEOS gelation catalyzed with D2000 as a function of the time interval of the acid prehydrolysis; $T = 23^\circ$C
D2000, which leads to increased ionization of the unreacted SiOH groups and acceleration of the polycondensation. The primary particles formed in the acid medium immediately grow by aggregation to form large clusters and the system gels. Fast gelation results in a chemical quenching and slowing down of the diffusion, thus leading to diffusion control of the reaction. The monomer is consumed during the first fast hydrolysis acid step, and only clusters are available for the polycondensation in the second step, thus allowing only the cluster-cluster reaction. The clusters show a more open structure, compared to the one-stage process. The fractal dimension is low, $D_m = 1.7$, and does not change during polymerization (see Fig. 1.5). Such a low value of the fractal dimension is consistent with the model of diffusion-limited cluster-cluster reaction, which can be effective in fast polymerization processes [49] such as this one. The polymer chains grow; however, their inner structure remains unchanged (no change of fractal dimension). This is in contrast to gradual structure densification in the case of monomer-cluster aggregation in one-step polymerization.

The compact structures similar to those prepared in the one-stage process are formed when the neutral DBTDL catalyst was used instead of TSA in the first step.
The higher fractal dimension of these gels may refer to a low efficiency of DBTDL to catalyze the hydrolysis. As a result, a high content of the unreacted monomer, TEOS, is present in the second reaction stage. The participation of the reaction between monomers and large clusters (monomer-cluster growth) is likely, leading to formation of the compact structures.

Both structure evolution and final morphology of the O–I networks synthesized by the simultaneous polymerization are determined by the early reaction stages. Nucleophilic catalysis of the sol–gel process in the beginning stage brings about a gradual densification of the silica clusters during polymerization and formation of a more compact structure. Acid catalysis in the early stage prevents change of the inner chain structure and development of the fractal dimension (densification) during the reaction, despite the second step being base-catalyzed.

**Sequential Polymerization**

The silica structures grow within the preformed epoxide network. During swelling of the network with a TEOS-H₂O-IP mixture at room temperature, the hydrolysis of TEOS takes place while increasing the degree of swelling. The sol–gel polymerization of TEOS within the network is catalyzed with the acid or DBTDL, because the
polyamine D2000 already incorporated in the epoxide-amine network is not efficient as a base catalyst. Hence, under acid catalysis, the hydrolysis is very fast, and the structure evolution resulting in small particles corresponds to the first acid stage in the two-stage “simultaneous” process. However, the polycondensation proceeds only at an increased temperature. Nevertheless, diffusion of TEOS into the sample is slow, compared to the rate of formation of small clusters, and therefore a gradient of swelling degree and silica content throughout the sample appear.

Morphology and Structure of Epoxy-Silica Networks

In most cases, the generated silica phase percolates through the system and the epoxy-silica interpenetrating network with bicontinuous phase structure is formed. Heterogeneous microphase-separated hybrid IPNs DGEBA-D2000-TEOS are optically transparent because of the small size of the silica domains and the solubilizing effect of the poly(oxypropylene) chain of D2000. Only BDMA-catalyzed systems are opaque. Three polymerization procedures used to prepare the networks lead to different morphologies of the O–I network characterized by SEM (Fig. 1.6), and to different structures of the silica determined by SAXS (Fig. 1.7).

The morphology of the network synthesized by the one-step base-catalyzed simultaneous polymerization is the most heterogeneous one. The hybrid involves large siloxane-silica aggregates with a size of ~100–300 nm, composed of smaller particles/clusters of 20–70 nm in diameter (see SEM micrograph in Fig. 1.6a). The silica structure is very compact, as is obvious from the steep intensity curve of the SAXS profile in Fig. 1.7. The fractal dimension in the dry hybrid reaches the value of $D_m = 2.7$.

The networks prepared by the two-step acid-base polymerization show smaller silica structures. The silica domains are of size 50–100 nm in Fig. 1.6b. The very fast polymerization and gelation of the siloxane phase in this case result in quenching of microphase separation in the early reaction stage, and in formation of a fine structure. The relative rates of polymerization and microphase separation play a crucial role for the final morphology. The dried system exhibits the two-length scale structure revealed from two linear parts in a double logarithmic plot of the SAXS profile shown in Fig. 1.7. The structure corresponds to large, loose polysiloxane aggregates of low fractal dimension, $(D_m)_{\text{aggregate}} = 2.0$, composed of smaller, more compact particles, $(D_m)_{\text{particle}} = 2.7$.

The finest morphology of the O–I network is created by the sequential polymerization with the preformed epoxide network. The small inorganic domains with a size of ~10–20 nm are formed, and no larger aggregates are observed in the SEM micrographs (see Fig. 1.6c). The content of SiO$_2$ in the hybrids increases with the fraction of TEOS in the TEOS-IP mixture; however, the size of the siloxane structures formed within the epoxide network does not grow with the silica content. The distribution of the inorganic phase is not homogeneous throughout the sample, due to a nonhomogeneous swelling of the epoxide network. The surface skin appears with a higher SiO$_2$ concentration, compared to that in the inner part.
Fig. 1.6 SEM micrographs of the hybrid DGEBA-D2000-TEOS prepared by (a) one-step polymerization, (b) two-step polymerization, including acid prehydrolysis of TEOS, (c) sequential polymerization with preformed epoxide network