Akademie věd České republiky

Teze doktorské disertační práce
k získání vědeckého titulu „doktor věd"
ve skupině věd chemických

Polymer networks – from „ideal" to organic-inorganic networks

Komise pro obhajoby doktorských disertací
v oboru makromolekulární chemie

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Praha, prosinec 2008

Introduction

The thesis involves study of the formation, structure and properties of polymer networks. The work deals with a broad range of the crosslinked polymers from simple "ideal" homogeneous networks up to complex nanostructured organic-inorganic (O-I) systems, and includes the investigation performed in the time period 1979-2007. The large part of our work was devoted to the epoxy networks, which is the most common thermoset system used for synthesis of adhesives, protective coatings, high-performance thermosets, etc. High requirements on material properties, however, lead to development of new polyfunctional materials. Heterogeneous multicomponent systems show often better properties than homogeneous ones. Therefore, in the last 10 years we have investigated nanostructured O-I networks displaying under optimum conditions synergy of properties of both phases, such as hardness or inflammability of the inorganic phase, and elasticity or toughness of the organic polymer.

The thesis is divided into three main parts. The first part describes the study of the chemistry of synthesis of the epoxy networks. This research includes determination of the *reaction mechanism of curing the epoxy systems* using different curing agents. The knowledge of the reaction mechanism is crucial in study of the epoxy networks. The second part deals with a *polymer networks formation* and description of the factors governing the network build-up, its structure and properties. The third part presents the theme related to the *heterogeneous O-I polymer networks*. In addition, a short paragraph is devoted to the study of special types of the networks showing *responsivity* to external stimuli.

Goal of our research consisted in understanding the processes at formation of polymer networks of various types including complex O-I networks and determination of general relationships between formation, structure and properties of the crosslinked systems. Optimization of the synthesis procedure and prediction of the thermoset material properties present the practical aim of the study.

The received knowledge about the polymer network formation was applied in study of the complex nanostructured O-I networks. Detailed characterization of the structure at various length scales and control of the morphology were the indispensable aspects in investigation of the network-based polymer nanocomposites. Development of new multicomponent polymeric materials based on the

heterogeneous O-I networks with improved mechanical and thermal properties was the final goal.

Results

Strategy of the networks investigation involves the following steps.

- *Reaction mechanism* governs formation of the network, as well as its structure and properties. We have determined the reaction mechanism and reaction kinetics by using low-functional models due to easier characterization of the reaction products, intermediates and a reaction path.
- *Molecular structure evolution* during *network formation*, including gelation and postgel structure evolution, as well as possible vitrification have been followed by chemorheology experiments, and by static and dynamic light scattering.
- *Phase structure evolution* during polymerization of the heterogeneous O-I hybrids has been determined in situ by SAXS and light scattering.
- *Structure* of the networks, *morphology* and *interface interaction* in the heterogeneous networks, as well as *thermomechanical and thermal properties* has been determined.
- *Theory of network formation* has been used to predict structure evolution, gelation and crosslink density. Data determined from the reaction mechanism and kinetic scheme served as input parameters.

Chemistry of epoxy networks synthesis – reaction mechanism

The epoxides are the most often used thermoset systems [1]. They could be cured with a great number of different curing agents in a wide range of temperatures thus providing an easy control of crosslinking density. Moreover, no volatiles are evolved at curing and a reaction shrinkage is small compared to vinyl polymerization. As a result, a high variety of material properties could be achieved by synthesis of the epoxide thermosets.

The knowledge of chemistry of networks synthesis is of main importance in investigation of the networks, and therefore determination of the reaction mechanism and kinetics of the epoxy curing represented an important part of our research. We have studied and described the mechanism of the reaction of the epoxides with carboxylic acids [A4, A10], acid anhydrides [A5], amines [A8, A11, A16, A17], anionic polymerization catalysts – tertiary amines or tertiary amino alcohols [A19, A24], cationic polymerization catalyst – BF_3-amine complex [A25, A30] and dicyandiamide [A18]. The most significant contribution to the general knowledge was achieved in the case of curing with amines, acid anhydrides and carboxylic acids.

Crosslinking of the epoxides with _polyamines_ is the most often used type of the epoxy curing. The addition reaction of the epoxy group with a primary amine is the main reaction and proceeds in two steps involving successive reactions of the primary and secondary amino group. In addition to these reactions also etherification takes place, which is initiated by the OH group formed in the epoxy-amine reaction. Usually, however, the epoxide homopolymerization by etherification is operative only in curing at excess of the epoxide, at a high temperature (T>150° C) and in the presence of a catalyst. Thus, the kinetics is described by two reaction constants of the addition of the primary and secondary amine.[2]

The mostly used epoxy resin is based on diglycidylether of Bisphenol A (DGEBA). In addition, the polyfunctional epoxides based on diglycidylamine derivatives are widely applied mainly in the synthesis of high-performance composites. Tetraglycidyl diamino diphenylmethane (TGDDM) is a typical epoxide used for the high T_g systems in such applications. However, while the mechanism of the reaction of DGEBA with amines is a simple one, as mentioned above, the mechanism of a reaction of diglycidylamine based epoxides with amines is more complex and not fully understood. Therefore, we have investigated the reaction mechanism of diglycidylaniline (DGA) curing. The specific features of the DGA derivatives are the steric proximity of two epoxy groups and presence of the tertiary nitrogen atom in the molecule providing an internal catalysis.

In the case of DGEBA the reactivity of both epoxy groups in the diepoxide are equal and independent.[3] The kinetics of the reaction with a primary amine is fully described by the relative rates of the
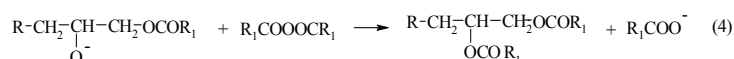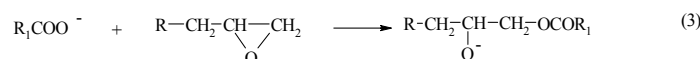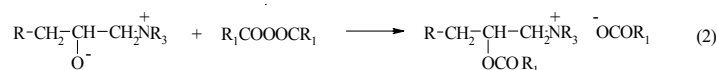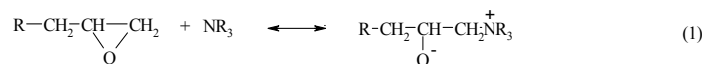
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primary and secondary amino groups (characterized as a substitution effect), which determines structure evolution during polymerization, gelation and final structure of the network. In contrast, we have proved in the papers [A14, A16, A17] that the reactivity of the epoxy groups in DGA derivatives are interdependent. The reaction of the first epoxy group brings about a local catalysis because the adjacent epoxy group is activated by the formed hydroxyl group. This internal catalysis leads to a positive substitution effect of epoxy groups in DGA. The kinetics DGA-amine thus involves the substitution effect in amine (often negative) and positive substitution effect of epoxy groups in DGA. We have determined also that a mutual dependence of reactivities of all functional groups is operative and four rate constants have to be taken into account in order to describe the kinetics of the reaction with a primary amine. Moreover, DGA-amine system shows a tendency to cyclization [4]. In the papers [A11, A15, A21] we have found that small 6-8 membered rings are formed in a high extent by intramolecular addition and etherification. This is in contrast to the reactions of DGEBA with amines. DGEBA is a rigid molecule and cyclization to form small rings is strongly prevented.[5]

The kinetic model based on the determined complex reaction mechanism of the DGA-amine system was used to simulate the structure evolution and the final network structure. Addition reaction diepoxide-amine with four interdependent rate constants, etherification, formation of small cycles and anionic polymerization (the mechanism described in [A37]) were taken into account in the model described in [A26].

Acid anhydrides are the next most important curing agents after amines. The curing without a catalyst is considered to be initiated by a proton donor present in a reaction mixture. In the presence of a base catalyst several mechanisms of the epoxide-anhydride reaction have been discussed. The reaction initiated with Lewis bases (tertiary amines) proceeds by chain-wise polymerization, however, still the mechanism was not fully elucidated. The initiation step of the reaction was the main problem. Three types of initiation were suggested: (a) ionic mechanism according to Fischer [6], (b) initiation by preexisting proton-donor [7] and (c) initiation by in situ formed proton-donor [8].

We have investigated the reaction mechanism of the reaction catalyzed with tertiary amines and determined initiation and formation

of active sites in the paper [A5]. The reaction scheme (eqs 1-4) was suggested.

$$R-CH_2-CH-CH_2 \;+\; NR_3 \;\longleftrightarrow\; R-CH_2-CH-CH_2\overset{+}{N}R_3 \qquad (1)$$
$$\;\;\;\;\;\;\; \underset{O^-}{|}$$

$$R-CH_2-CH-CH_2\overset{+}{N}R_3 \;+\; R_1COOOCR_1 \;\longrightarrow\; R-CH_2-CH-CH_2\overset{+}{N}R_3 \;\;^-OCOR_1 \qquad (2)$$
$$\underset{O^-}{|}\; \underset{OCOR_1}{|}$$

$$R_1COO^- \;+\; R-CH_2-CH-CH_2 \;\longrightarrow\; R-CH_2-CH-CH_2-OCOR_1 \qquad (3)$$
$$\;\;\;\; \underset{O^-}{|}$$

$$R-CH_2-CH-CH_2-OCOR_1 \;+\; R_1COOOCR_1 \;\longrightarrow\; R-CH_2-CH-CH_2OCOR_1 \;+\; R_1COO^- \qquad (4)$$
$$\underset{O^-}{|}\; \underset{OCOR_1}{|}$$

The reaction mechanism involves the initiation step (eqs 1 and 2) in which the tertiary amine is irreversibly chemically bound. The amine reacts first with the epoxide to form zwitterion and an alkoxide anion (1) which is followed by the reaction with the anhydride under formation of a quaternary ammonium salt involving a carboxy anion (2). In the later stage the reaction proceeds without participation of the tertiary amine. The carboxy anion opens the epoxy ring (3) and the arising alkoxide reacts with anhydride to form the diester (4). Simultaneously the RCOO$^-$ anion is regenerated and starts a successive repetition of the steps in eqs 3 and 4. The proposed mechanism has proved that presence of a proton-donor preexisting in the reaction mixture or in situ arising is not necessary for initiation of the epoxy-anhydride reaction.

The reaction between an epoxide and a *carboxylic acid* proceeds by addition esterification, accompanied by side reactions like condensation esterification, etherification and hydrolysis of the epoxide.[9] In the base (tertiary amine) catalyzed system the addition esterification to form monoester is the only reaction in case of the equimolar mixture. It is followed by etherification or condensation esterification only at a nonequimolar composition after consumption of the minority groups, i.e. carboxyl or epoxide groups, respectively. However, we have found and described in the paper [A4] that also another reaction, *transesterification*

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of the monoester to form diester and glycol, takes place This reaction occurs even in the equimolar system and proceeds even after full conversion of both functional groups. In the bi- (diepoxide-diacid) and polyfunctional systems this reversible transesterification leads to a simultaneous breaking the chains (sequence of monoesters) and giving rise to new crosslinks (diester unit). As a result, gelation occurs in the equimolar bifunctional systems and a network structure is significantly affected in the polyfunctional systems due to transesterification. The occurrence of this reaction is important in the preparation of rubber-toughened epoxies by using carboxyl terminated polybutadienes.

Polymer network formation, structure and properties

The results, obtained at study of the reaction mechanism and kinetics using the low-functional models, were employed at investigation of the crosslinking of polyfunctional systems to form polymer networks.

During the nonlinear polymerization of a polyfunctional system [10,11] the molecular structure grows and polymer branching occurs finally reaching the point of gelation. At this moment mass average molecular weight, M_w, and viscosity diverge and a giant macromolecule, gel, appears in the system. In the postgel stage both fraction of the gel and crosslinking density of the network grow, which is accompanied by build-up of elasticity of the system characterized by increase in the elastic modulus.

We have followed and described molecular structure evolution during network formation, including gelation and vitrification of the system, in the papers [A23, A25, A40, A43].

Gelation

Gelation, i.e. transition from the liquid to solid state, is the key phenomenon during the network formation as it is the crucial moment from the point of view of processability of the cured system. Determination of the gelation point (GP) is of the highest importance both from practical and theroretical aspects. The most convenient method to follow formation of the network and to detect the GP is chemorheology. This technique monitors in situ changes in the rheology of the system during the whole path of the chemical reaction, and thus

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evolution of the structure, from the reaction beginning through the gelation up to the full conversion in the postgel stage.

During polymerization, the viscous properties are dominant in the pregel, liquid state, i.e., the dynamic loss modulus (G'') is larger than storage modulus (G') and loss factor tan δ ($=G''/G'$) >1. On the contrary, the elastic properties are dominant in the solid state beyond the GP, where $G'' < G'$, and tan δ<1. Consequently, the crossover of the dynamic storage and loss moduli during polymerization, i.e. tan δ=1, was often assumed as corresponding to GP [12]. Winter and Chambon [13] described the procedure of determination of GP based on the rheological properties of the system in the critical state. The critical gel shows a self-similar rheological behavior which is expressed in universal simple power law relaxation of the modulus. Accordingly, the gel point is experimentally detected as a moment when tan δ becomes independent of the frequency in the dynamic measurement.

We have found that in the case of the epoxy-amine system (DGEBA-polyoxypropylenediamine) the reaction time to reach tan δ = 1 is dependent on the experimental frequency [A23], thus proving that the crossover of the moduli ($G'(t)=G''(t)$) does not coincide with the gel point. We have shown that the critical value at GP (tan $\delta)_C$ depends on the conditions of the network formation and a polymer structure in the critical state. Long primary chains existing (formed) in the pregel stage result in formation of entanglements before GP leading to a higher storage modulus at a given frequency and a lower tan δ at GP. The paper [A23] shows that gelation manifests itself also by a sudden generation of a negative normal force in the dynamic mechanical experiment. This effect was interpreted as a result of volume contraction during polymerization and an appearance of equilibrium elasticity beyond the GP leading to drawing up the rheometer plates together in case of a good adhesion between the polymer and the rheometer plate

The rheological determination of the gel point becomes a difficult problem in systems vitrifying closely after gelation. Both processes, gelation and vitrification, were found to interfere and rheological behavior in the GP was not independent of experimental frequency [A43].

Onset of *vitrification* has been followed by chemorheology and described in the papers [A25, A43]. Vitrification manifests itself by a local minimum in the loss factor tan δ during polymerization and by the

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second crossover of the loss factor curves for different experimental frequencies. During vitrification, strong viscoelastic effects operate, characterizing chain immobilization. As a result, the loss factor increases during the cure reaching the local maximum. In the glassy state then $G''(t)$ declines and tan δ reaches a very low value. Because of slow relaxation modes and broad relaxation spectrum in the glass transition region, the loss factor decreases with increasing frequency in a similar way as in the viscous liquid state and in contrast to the elastic solid state, thus resulting in the crossover.

Network formation – effect of the reaction mechanism

The point of gelation characterized by time of gelation or by critical conversion at the gel point, α_C, reflects the path of network formation. It is determined by the reaction mechanism, the types and functionalities of reagents, composition of the system, etc. Under ideal random polymerization the critical conversion is given by functionality of the monomer, f (eq.5) [14]. The ideal system is defined by homogeneity, i.e., by uniform distribution of functional groups in the volume, by equal reactivity of all functional groups, absence of intramolecular reactions (cyclization) and of the diffusion control of the reaction.

$$\alpha_C = (f-1)^{-1} \tag{5}$$

The critical point serves as a sensitive characteristic of the *reaction mechanism* and of the deviations from the ideal system. The deviations from the ideality are manifested in the network formation by shift of the critical conversion.

Cyclization and unequal reactivity of functional groups are the most common examples of the nonrandom effects in the reaction. *Cyclization* (intramolecular reaction), in contrast to the intermolecular reactions, does not contribute to a growth of the molecular structure during polymerization. Probability of cyclization Λ_C is given by expression (6) [15]

$$\Lambda_C = B/C \qquad\qquad B = (3/2\, \pi n b^2)^{3/2}, \tag{6}$$

where C is concentration of functional groups, b is the effective bond length characterizing a structure flexibility, n is the number of bonds in the smallest ring. Extent of cyclization increases with dilution (C^{-1}), flexibility of a structure and decreasing size of the corresponding ring. The cyclization manifests itself by a shift of the critical conversion to a

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higher value. The measure of cyclization, therefore, could be characterized by a slope of the dependence α_C on dilution.[5] Effect of *unequal reactivity* of functional groups on the gel point is well demonstrated in the epoxy-amine reaction. When the reactivity of the secondary amine is lower than that of the primary amine, i.e. negative substitution effect is operative, the linear chains are formed in the early reaction stage and only later branching and crosslinking occur. As a result, the gel point is delayed and the critical conversion is higher compared to the random case.

Characterization of gelation by the conversion at the gel point, α_C, often suffers from experimental difficulties to determine α_C because of instability of the system in the critical state. In order to avoid this problem we have used another approach by studying fully cured stable off-stoichiometric networks and determining the *critical molar ratio* of functional groups [5]. In the case of the networks formed by ideal alternating copolymerization of reagents R_A and R_B with A and B functionalities (e.g. epoxy-amine networks), the highest crosslinking density is achieved in the stoichiometric, i.e. equifunctional, composition (molar ratio of functional groups $r_A = [A]/[B] = 1$). The fraction of the sol increases and crosslinking density decreases in the off-stoichiometric networks with increasing excess of any functionality. The critical molar ratio of functional groups r_C is the ratio necessary for gelation. At the system composition corresponding to r_C the gelation occurs just at the complete conversion of the minority groups. No gel is formed at a higher ratio, $r_A > (r_A)_C$ in case of A being in excess.

For an ideal case it holds : $(r_A)_C = (f_A-1)(f_B-1)$ (7)

In the same way as the critical conversion also the critical ratio r_C characterizes mechanism of the network formation and deviates from the ideal value in eq.7 as a result of cyclization and unequal reactivities of functional groups, etc. By using the *critical molar ratio method* we have studied formation of the networks in the papers [A3, A9, A13, A22, A35] and determined the effect of the reaction mechanism on the network build-up and the structure.

Polyurethane network

We have prepared the off-stoichiometric polyurethane networks from poly(oxypropylene) triol (PPT) and diol (PPD), trimethylolpropane (TMP) and diphenylmethanediisocyanate (MDI) [A3]. The cyclization

in the network, PPT-MDI, characterized by the slopes r_C vs C^{-1} plots, was proved to increase with decreasing size of the formed ring, i.e., the molecular weight of the PPT, in agreement with eq.6. However, very weak cyclization, manifested by independency of r_C on dilution, occurs in the ternary system PPD-TMP-MDI. In this case, the formation of stiff clusters of TMP-MDI units prevents cyclization due to low chain flexibility. The effect of cyclization was eliminated by nonlinear extrapolation of r_C to zero dilution and the extrapolated value of the critical ratio, corresponding to the ring-free case, characterized the effect of unequal reactivity of functional groups. The ternary system PPD-TMP-MDI contains two types of OH groups; the more reactive primary OH in TMP and less reactive secondary ones in PPD. On the contrary, all functional groups (secondary OH) in the system PPD-PPT-MDI are equireactive. Due to a higher reactivity of the OH groups of the crosslinker (TMP) the former system gels earlier, at a lower critical conversion, and at a higher critical ratio r_C (= [OH]/[NCO]) (with OH groups in excess), i.e. at a more off-stoichiometric composition.

Epoxy-amine networks

The formation and structure of amine cured epoxy networks based both on DGEBA and DGA (TGDDM) type monomers were studied. The complex investigation involved determination of the reaction mechanism and the reaction kinetics using the monofunctional models, study of the linear polymer growth from the bifunctional monomers described in [A27], and the network formation in the polyfunctional system studied in [A9, A13, A20, A22, A35], including the theoretical prediction of the kinetic model [A26]. Moreover, theory of network formation used to describe the structure growth in the network was modified in [A35] to include a complex mechanism of the DGA-amine reaction.

We have shown that the difference in reaction mechanisms in the DGEBA and DGA systems affects the structure growth and the final network properties. Build-up of the linear and branched structures in the pregel stage, followed using the bifunctional models (diepoxide-monoamine) in [A27], is much slower in the case of DGA. The molecular weights of the linear polymers DGA-aniline are by an order of the magnitude lower compared to DGEBA-aniline due to formation of a high amount of small cycles. Also DGA(TGDDM) -amine network

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formation was proved to be mainly affected by the *short range cyclization* as the critical ratio strongly depends on dilution [A22, A35]. As a result, the corresponding networks show a high sol fraction w_S (containing small cyclic products) even in the completely reacted stoichiometric network and a lower crosslinking density determined from rubbery modulus, compared to the DGEBA networks [A35]. On the contrary, in DGEBA based networks the r_C value is independent of dilution revealing absence of cyclization in agreement with literature. [5] The stoichiometric networks show $w_S \rightarrow 0$ and the system is close to be ideal. Only curing with long flexible poly(oxypropylene)diamines (Jeffamines) results in a high extent of cyclization and increased sol fraction in the DGEBA-Jeffamine networks [A12, A35].

Networks formed by the initiated chain-wise reaction mechanism

In addition to the polyurethane and epoxy-amine networks representing the typical systems formed by step-growth polymerization, we have studied the networks built by initiated chain-wise polymerization, i.e. by ionic [A7,A25,A30], free-radical [A28] and ring-opening polymerization [A6].

Two different reaction mechanisms are operative in the *curing of an epoxide with acid anhydrides* and *carboxylic acids* under catalysis with tertiary amines. In the paper [A7] we have shown how the reaction mechanism determined the structure of the growing polymer and of the network. Of a high importance is the fact that at curing of the epoxide with anhydrides the tertiary amine is irreversibly bound as determined in [A5] and serves as an initiator of the *anionic chain-wise polymerization*. The molecular weight of the linear polymer products in the case of the "initiated mechanism" of monoepoxide-cyclic anhydride system decreases with increasing concentration of tertiary amine. On the contrary, in the "step-wise mechanism" of the reaction of diepoxide with a carboxylic acid the tertiary amine is quickly regenerated and molecular weight of the formed polyester is independent of the content of the tertiary amine acting as a catalyst in this case [A7].

Cationic polymerization of DGEBA initiated with BF$_3$-methoxyaniline complex in the presence of χ-butyrolactone (BL) is another initiated polymerization studied in the papers [A25,A29,A30]. Also in this case, the product properties depend on concentration of the

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initiator as its high content leads to increasing number of chain ends and to lower molecular weights. Formation of shorter primary chains with a lower effective functionality given by the number of DGEBA units results in increase in the critical conversion and lower crosslinking density of the network, corresponding to a decrease in rubbery modulus G_e and T_g. Too low content of the initiator, however, leads to an incomplete conversion, a low crosslink density as well as Tg or even absence of gelation due to termination reactions. Reactive diluent BL promotes an increase in the critical conversion because of the spiro orthoester formation[16] which competes with homopolymerization of the epoxide.

Free-radical copolymerization of bismaleimides with styrene [A28] shows a significant increase in the gel point conversion ($\alpha_C > 0.2$) compared to theoretical ring-free crosslinking radical polymerization due to cyclization and steric inaccessibility of pendant double bonds inside the microgels.

Ring opening polymerization of dicyclopentadiene (DCP) by using the Ziegler–Natta type catalyst (WCl_6 – diethylaluminium chloride) has been described in the paper [A6]. The polymerization takes place without a significant consumption of double bonds implying that the reaction proceeds by the metathesis. Very low critical conversion ($\alpha_C < 0.01$) proved an initiated chain-wise mechanism. The reaction is initiated by ring opening polymerization of the more strained norbernene ring of the DCP monomer. Long linear chains with pendant functionalities (cyclopentane rings) are formed at an early reaction stage. Gelation then occurs at low critical conversion by crosslinking the long chains through the cyclopentane rings. The extremely fast exothermic reaction is suitable for reaction injection molding (RIM) polymerization technique. Due to a high exotherm during polymerization the networks with a high Tg and crosslink density are formed at room temperature. However, we have found that the specific temperature range within the sample exists for optimum properties of the cured material. Deterioration of properties (decrease in crosslink density and Tg value as well as increase in sol fraction) occurs at a high temperature due to a faster deactivation of catalytic centers and a reverse cyclodegradation.

Theory of network formation

Theories of network formation describe evolution of the branched structures during polymerization, gelation of the system and evolution of the structures in the postgel stage. Statistical [17-19] and kinetic [20] theories as well as computer simulation [21] in space are developed to describe network formation. We have applied theory of branching processes (TBP) developed by Gordon [17] and Dušek [18] and combined kinetic-statistical model to predict the structure evolution, gelation and the final network structure in several complex epoxy systems [A35, A22, A29, A30].

DGA-amine network

The theoretical statistic TBP model for epoxide-amine networks was modified in [A35] to include full complexity of the reaction mechanism of curing DGA based epoxies with amines and the kinetic model as determined by us in [A26]. The model properly describes formation of the network and structural parameters both in the stoichiometric and off-stoichiometric networks with both amine and epoxide excess. In addition to short range cyclization by intramolecular addition and interdependent reactivities of epoxy and amino groups also the intramolecular etherification and homopolymerization by etherification and ionic polymerization, as well as formation of reactive intermediates were taken into account in the model.

Cationic polymerization of DGEBA

The theoretical treatment of network formation by cationic crosslinking polymerization is lacking. The cationic curing of polyepoxides is an initiated reaction and the structure growth is affected by its history, i.e., the long-range correlation effects are present. Consequently, the statistical theories of network formation cannot provide a rigorous solution and a full kinetic treatment has not been yet applied. We have developed in the papers [A29,A30] the theory of network formation for cationic polymerization of DGEBA based on a combination of kinetic theory and statistical TBP. The combined model consists in a kinetic generation of linear clusters in the first step followed by their recombination using a statistical method to form branched structures and a network in the next step. The determined complex reaction model including several modes of initiation, propagation, chain transfer and

termination as described in [A25] was used as an input parameter for calculation of distribution of linear clusters. Moreover, the reactions of the reactive solvent, χ-butyrolactone, to form the spiro orthoester and corresponding copolymers with DGEBA, were included in the theoretical model. The theory predicts well structure evolution during polymerization characterized by polymer fraction, gelation, increase in fraction of the gel and crosslinking density.
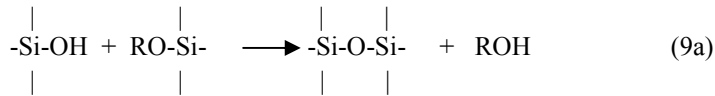

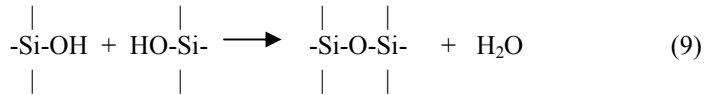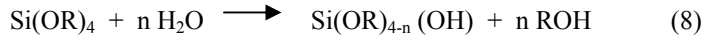## Organic-inorganic polymer networks

Introducing an inorganic phase into a polymer leads to a heterogeneous composite material. According to the size of heterogeneities one can define microcomposites (classical composites), nanocomposites and molecular composites, i.e. hybrids. The O-I polymers are classified as the hybrids or nanocomposites because they contain organic and inorganic components blended in a single system on the molecular or at least nanoscale level. Under optimum conditions, the O-I polymers show synergy of properties of both phases like hardness, strength or inflammability of the inorganic phase and elasticity, toughness and good processability of the polymer. Moreover, the systems exhibit optical clarity due to small size of inorganic nanodomains.

The polymer networks often serve as an organic matrix of the O-I hybrids. An inorganic component, mainly the Si, Ti, Sn or Al-based compounds, represents a filler dispersed in a polymer to form O-I networks of various morphologies. Hydrodynamic effect of a hard filler, interaction polymer-filler and possible inorganic phase percolation in the polymer matrix result in reinforcement of the polymer. Generally, structure and morphology as well as uniformity of dispersion of the inorganic phase in an organic matrix are important characteristics determining properties of the heterogeneous systems[22,23]. Particularly, the nanocomposites with a very fine morphology and microphase separated nanosized (1-100 nm) inorganic domains display excellent mechanical, thermal and scratch resistant properties.

Control of the mixing of two dissimilar phases is a critical problem in synthesis of the O-I nanostructured polymers. The convenient procedure of formation of O-I polymers is based on the *sol-gel process*. It provides an easy way of incorporation of an inorganic phase into an organic matrix under mild reaction conditions. Moreover,

this polymerization technique overcomes the problems with a difficult dispersion of inorganic "filler" because precursors of an inorganic phase are initially dispersed on a molecular level in an organic matrix.

The *sol-gel process* consists in hydrolysis (8) and condensation (9) of metal alkoxides (Si, Ti, Al, Sn). [24] Mainly alkoxysilanes are used as precursors to generate inorganic structures and tetraethoxysilane (TEOS) is the most common monomer to form silica network in situ within an organic matrix.

$$Si(OR)_4 + n\,H_2O \longrightarrow Si(OR)_{4-n}(OH) + n\,ROH \qquad (8)$$

$$-Si\text{-}OH + HO\text{-}Si- \longrightarrow -Si\text{-}O\text{-}Si- + H_2O \qquad (9)$$

$$-Si\text{-}OH + RO\text{-}Si- \longrightarrow -Si\text{-}O\text{-}Si- + ROH \qquad (9a)$$

The inorganic phase domains formed by the sol-gel process in the O-I networks are polydisperse in size and heterogeneous in chemical composition. Better characterized nanostructured O-I polymers are prepared using well defined inorganic nanobuilding blocks (NBB) with predetermined molecular architecture. A large variety of organofunctional NBB are studied, however the main research activity in this field is devoted to polyhedral oligomeric silsesquioxanes (POSS). POSS are cluster-like oligomers of the general formula $(RSiO_{3/2})_n$, represented mainly by the cage-like octamer derivatives [25]. The POSS molecule in Fig. 1 involves a core-shell nanosystem with the compact Si-O core as a thermally stable robust framework and a shell of organic substituents. These substituents control the miscibility of the POSS with an organic matrix. The functionalized POSS, i.e., POSS unit with the reactive substituents, is suitable for incorporation into a polymer.[26]
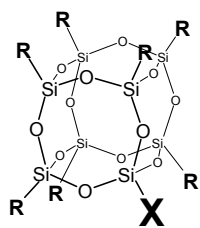
Figure 1 Polyhedral oligomeric silsesquioxane – POSS.
R – organic substituents, X – reactive substituent

These three-dimensional cages of the size ~ 5-25 Å in diameter are comparable to size of polymer segment dimensions and resembles a nanosized particle SiO_2. Hence, a local reinforcement and immobilization of a polymer chain takes place. The POSS-polymers show an improvement of properties, such as increased Tg, modulus, decomposition temperature, reduced flammability and increased gas permeability. Literature data, however, display that the effect of incorporation of POSS in the polymer is by far not unequivocal. Both increase and decrease as well as no change of T_g were reported in various POSS-polymers. The effect of POSS on the chain dynamics and polymer reinforcement is still not answered. The properties, structure and morphology of the POSS-polymer hybrids is determined by strength of two types of competing interactions between POSS and polymer (POSS-chain interaction) and between POSS units (POSS-POSS interaction). The latter interaction results in tendency of POSS to phase separate and to form the POSS aggregates. Lichtenhan et al. [27] assume that aggregation of POSS units have a dominant effect in controlling the physical properties of POSS-modified polymers. On the contrary, Bhardawaj [28] showed that the anchoring effect of a large mass POSS molecule bound to the chain is responsible for slowing down the chain dynamics without necessity of POSS aggregation.

Phase or microphase separation during network formation leading to heterogeneous hybrids is a typical feature of the O-I networks. Therefore, determination of phase structure evolution in the polymerization and a proper characterization of the hierarchical structure and morphology are the main experimental objectives in the investigation of the O-I polymer systems. In addition to the size of the

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heterogeneity domains we have applied also the geometrical description of the structures using the concept of fractal geometry because random processes of polymerization or aggregation usually lead to formation of fractal objects.

Strategy of our investigation of the O-I networks and description of the results is given in [A36] and [A47]. In our research we have tried to find an answer to the following general problems related to the nanostructured polymer networks: How the material properties are affected by morphology? What is the effect of size and shape of inorganic nanodomains, their topological arrangement and space distribution in the polymer matrix ? Of importance are the effects of chemical bonding of inorganic structures to the polymer and strength of interface interaction as well as the effect of supramolecular structure on the nanocomposite properties ?

Control of the hybrid structure and morphology on various length scales is a crucial point in synthesis of the O-I networks. We have prepared and studied the hybrids of various morphologies – the networks with inorganic phase nanodomains dispersed within the organic matrix, the networks with bicontinuous phase structure, the networks with ordered inorganic phase as well as the O-I block copolymer networks with inorganic junction domains.

Two types of organic-inorganic networks have been investigated
- Networks with in situ formed inorganic phase
- Networks with defined inorganic nanobuilding blocks

O-I networks with in-situ generated silica phase

The organic matrix was composed of the rubbery epoxy network from DGEBA and poly(oxypropylene)diamine (Jeffamine D2000). The inorganic silica phase was formed in situ in the polymer by the hydrolytic polycondensation of TEOS. We have prepared the hybrid network (DGEBA-D2000-silica) by the simultaneous polymerization of organic and inorganic monomers or by the sequential procedure (Figure 2). The O-I network structure and morphology were controlled by reaction conditions, mainly by catalysis of the sol-gel process (acid catalysis, basic catalysis with amine D2000 or pH neutral catalysis with dibutyl tin dilaurate (DBTDL)), by molecular architecture of the

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organic-inorganic precursor, by polymerization procedure and by grafting of the O-I interphase.
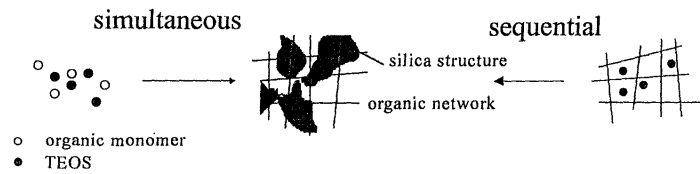

Figure 2 Synthesis procedures of the epoxy-silica network with in situ generated silica phase

Simultaneous polymerization

Simultaneous build-up of epoxy and silica networks proceeds by two independent reaction mechanisms. In the papers [A31, A32] we have followed evolution of both epoxy and silica structures by DMA and SAXS. The monomers were initially molecularly dispersed but during polymerization microphase separation occurred and the nanostructured polymer appeared.

One step polymerization of the system DGEBA-D2000-TEOS proceeds under base catalysis of the sol-gel process with the oligomeric amine (D2000). Such conditions result in the reaction limited monomer-cluster aggregation of the silica structures and a slow gelation to form interpenetrating epoxy-silica network. The silica clusters show fractal behavior and their structure is characterized by fractal dimension D_m. During polymerization the fractal dimension gradually increases, corresponding to densification of the structure. The final high value, $D_m=2.7$, reveals quite compact structure in agreement with the monomer-cluster type aggregation. The hybrid morphology includes heterogeneous silica aggregates of the size ~ 100-300 nm composed of smaller particles (20-70 nm in diameter)

The sol-gel reaction is efficiently accelerated in the *two-step polymerization* procedure consisting in the acidic prehydrolysis of

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TEOS in the first stage followed by base catalyzed (with D2000) polycondensation in the second step. Fast hydrolysis in the 1st step leads to formation of small particles of the size ~ 2 nm. In the 2nd base catalyzed step the rapid aggregation of primary particles and formation of large clusters takes place. As a result, a very fast gelation of the silica phase occurs. Rapid polymerization and gelation leads to quenching of microphase separation in the early reaction stage and in formation of a fine morphology. The silica domains are of the small size, ~ 50-100 nm. The aggregates show an open structure with a low fractal dimension, D_m=2.0, as a result of diffusion limited cluster-cluster aggregation mechanism.

The studied O-I hybrids undergo the polymerization induced phase/microphase separation. Therefore, the relative rates of polymerization and microphase separation, and their control, play a crucial role for the final *morphology of the interpenetrating O-I network.*

Sequential polymerization

The sequential procedure involves the hydrolytic polycondensation of TEOS within the preformed epoxy network. The sequentially prepared O-I networks display the finest morphology with small silica clusters of the size ~ 10 nm. In this case, the steric restrictions are the main reason of such morphology. Aggregation of the small silica particles and formation of larger aggregates is prevented within the rigid epoxide network.

In addition to the kinetic and steric factors, the *hybrid morphology* is strongly dependent on an *interaction between both phases*, which is controlled by the reaction mechanism. The acid catalyst of the sol-gel process promoting the fast hydrolysis results in silica structures in the O-I networks containing a high amount of silanols. On the contrary, base catalysis accelerates polycondensation while hydrolysis is slow and the content of silanols is very low [A31]. Presence of silanols in the silica structures leads to chemical grafting between phases by the reaction with C-OH of the epoxide network and to physical H-bond interaction with C-O-C structures of the polyoxypropylene chain of D2000 diamine. Therefore, the networks prepared under acid catalysis show more homogeneous morphology.

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This is the case of the simultaneous two-step polymerization with the acid prehydrolysis.

Thermomechanical properties and interphase interaction

In situ generated silica structures form hard glassy domains in the rubbery epoxy matrix and serve as nanofiller. We have proved in [A33] that a relatively small amount of the in-situ formed silica structures results in a significant reinforcement and the corresponding hybrids show higher moduli than the classical composite with Aerosile containing the comparable amount of filler.

The reinforcement, characterized by increase in shear storage modulus G' (T) in the rubbery region, depends on the way of the hybrid synthesis. The most efficient reinforcement was achieved in the O-I hybrids prepared by the sequential and by the two-step polymerizations. The „sequential" nanocomposite containing 6.9 vol% of the generated silica shows the rubbery modulus by two orders of the magnitude higher compared to the reference DGEBA-D2000 network. These two types of the O-I hybrids also reveal a very strong interphase interaction between the organic network and the glassy silica domains resulting in immobilization of the network chains.

The *interphase interaction*, governing to great extent mechanical properties, has been quantitatively described by fraction of the immobilized epoxy matrix and determined by using DMA [A33]. Formation of the immobilized interphase layer of the epoxy network in contact with the silica phase manifests itself in DMA by a new relaxation peak at a high temperature.

When treating the mechanical properties of the O-I networks we have taken into account the effective fraction of the hard phase, $v_{eff} = v_{Si} + v_{Ebg}$, including both the silica phase (v_{Si}) and the immobilized (bound) epoxide (v_{Ebg}). However, only the bound epoxy phase in the glassy state (v_{Ebg}) is active as hard filler. It implies that the strong interaction, leading to an increase in T_g of rubbery matrix above the room temperature, is necessary to enhance the effective filler fraction. The thickness of the glassy interphase layer is proportional to the strength of interphase interaction characterized by parameter $K = v_{Ebg} / v_{Si}$. The strength of interphase interaction and volume fraction of the interphase are dependent on the reaction mechanism and procedure of

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the O-I network synthesis. As shown above, the strong interaction is promoted in the networks formed under acid catalysis (two-step polymerization) and moreover, very fine morphology, i.e. small size (sequential polymerization) and open structure of the silica domains, favors the interaction with the epoxide network. On the contrary, grafting is weak in the case of networks prepared by base catalyzed one-step polymerization.

Elastic modulus of the two-phase system depends on the moduli and volume fractions of components as well as on morphology. The Kerner model modified by Nielsen (model Halpin-Tsai-Lewis-Nielsen) [29] is frequently used to predict the mechanical behavior of particulate composites. We have proved in [A33] by the analysis of DMA results and application of composite models of mechanical properties that the models of particulate composites did not fit the experimental data. The O-I hybrids with in situ generated silica form interpenetrating networks with two co-continuous phases involving dispersed particles of the inorganic sol. The equivalent box model (EBM)[30,31] and Davies[32] empirical model were used to treat the effect of phase continuity on dynamic mechanical properties. The volume fraction of the continuous silica phase $(v_{Si})_{cont}$ in the epoxy-silica hybrid was determined using the percolation theory.

$$(v_{Si})_{cont} = [(v_{Si} - v_{Sicr}) / (1 - v_{Sicr})]^t \qquad (10)$$

where v_{Sicr} is the critical volume fraction for a partial silica phase continuity and t is the critical exponent ($t=2.0$ [33]). For the chemical networks with covalent bonds the critical fraction is expected to be close to zero with exception of more heterogeneous base-catalyzed systems with lower phase continuity. In this case $v_{cr} = 0.02$ fits the experimental data.

The expression for the composite modulus (G_C) of the O-I networks involves the influence of effective fraction of the hard phase, strength of the interphase interaction and bicontinuous phase morphology.

$$G_C \approx [(v_{Si} - v_{Sicr}) / (1 - v_{Sicr})]^t (G_{Si} + KG_{Eg}) \qquad (11)$$

where G_{Si} and G_{Ebg} are moduli of silica phase and glassy modulus of the epoxide approximating the immobilized epoxide layer in the glassy state.

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O-I networks with well characterized interphase bonding

The epoxy-silica networks with the silica phase formed by hydrolytic polycondensation of TEOS show grafting of the epoxy chains to the hard silica structures. Strong interphase interaction includes both covalent bonds and H-bond interactions, however, this bonding is not well defined. Therefore, we have synthesized and studied the O-I networks containing well characterized interphase covalent bonding in order to understand the effect of interphase interaction on morphology and properties. The organofunctional alkoxysilane derivatives as coupling agents have been used to improve and control the covalent interaction between organic and inorganic phases. These O-I precursors contain both organic functional groups capable of polymerization or a reaction with a polymer, and the alkoxysilyl groups undergoing hydrolytic polycondensation to form an inorganic structure.

The *sol-gel polymerization of trialkoxysilanes* results in formation of silsesquioxanes (SSQO) of the structure $(RSiO_{3/2})_n$. The structure evolution during polymerization of the tri-functional monomers was described in [A32, A34, A37]. In the case of glycidyloxypropyl trimethoxysilane (GTMS), as the most common coupling agent for epoxy systems, the acid catalysis leads to gelation and build-up of the SSQO network, while the base catalyst promotes a high extent of intramolecular condensation reactions producing low-molecular weight polyhedral cyclics. The reaction mechanism is affected also by character of the organic substituent R, i.e. by its length and bulkiness. The trialkoxysilanes containing a short R substituent quickly gel independent of catalysis. On the contrary, a long substituent, e.g. in octyltrialkoxysilane, shields the alkoxysilane groups and prevents the intermolecular condensation from sterical reasons. As a result only the stable, mainly cage-like, octamer is formed by extensive intramolecular condensation and no gelation occurs.

We have studied the O-I networks with the SSQO structures covalently attached either at the chain end, thus forming the network junctions of the O-I block copolymer network, or grafted along the chain of the network.

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Two synthesis approaches, using two different O-I precursors, were applied to prepare the O-I block copolymer networks as described in the papers [A36, A38, A39] (Figure 3).
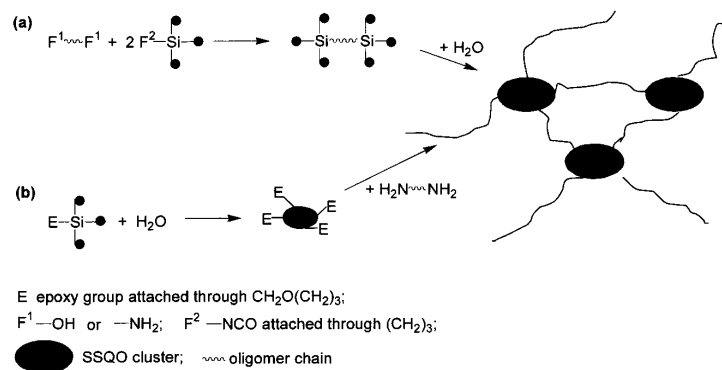

Figure 3   Formation of the O-I block copolymer networks from (a) alkoxysilane endcapped oligomers and (b) epoxy-functional SSQO clusters

The procedure (a) consisted in preparation of the *alkoxysilane endcapped oligomers (ASO)* followed by the sol-gel process of the alkoxysilane terminal groups to form SSQO junction domains at the chain extremities. According to the procedure (b) the epoxy functional SSQO domains (*epoxy functional cluster - EC*) were prepared first and then interlinked with an oligomeric (polyoxypropylene) diamine to build the O-I network. The two synthesis procedures involving different reaction mechanisms of the crosslinking reactions, lead to a different kinetics of formation and different structure and morphology of the networks.

The *ASO-based networks* are crosslinked by hydrolytic condensation, and hence formation and structure of the networks are governed by factors crucial for the sol-gel process. The hybrids contain small SSQO clusters of size 1-2 nm as network crosslinks. These SSQO

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junctions are highly condensed compact cage-like structures in case of base catalysis. The networks prepared under acid catalysis involve the crosslink domains of less compact loose SSQO clusters, containing linear siloxane sequences and a high amount of the unreacted SiOH.

In the *EC-based networks* two independent reaction mechanisms operate in crosslinking of EC with diamines. The early reaction stage is dominated by the sol-gel reactions leading to growth of the EC under base catalysis with the present oligomeric diamine, followed by the epoxy-amine reaction, which is the main crosslinking process resulting in gelation. The structure evolution and morphology are controlled by composition of the system, i.e.ratio of the EC and oligomeric amine. The microphase-separated networks of the stoichiometric composition show spherical domains composed of polyhedral cage–like SSQO structures of the size 5-15 nm. However, at excess of the epoxy clusters, the O-I network shows the ordered ladder–like SSQO structure containing interconnected SSQO cylinders and displays two percolation thresholds corresponding to the epoxy-amine O-I block copolymer network and the neat SSQO network.

The block copolymer O-I networks are well ordered and show a regular arrangement of the SSQO junction domains [A38]. The distance between the SSQO crosslinks correlates with the length of the linking oligomer chain.

The O-I networks from the alkoxysilane endcapped oligomers contain only a small amount of the inorganic phase (< 4 wt % in case of the precursor of M~2000). Increase in the content of inorganic domains in the network was achieved by addition of TEOS. These networks showed a disappearance of the regular arrangement and formation of the continuous silica structure at a high TEOS content [A39].

Elastic modulus of the block copolymer O-I networks

The block copolymer O-I networks (ASO networks and the stoichiometric EC networks) show only a slight increase in modulus with respect to the inorganic phase free reference systems due to a low content of the SSQO nanofiller and a relatively weak interphase interaction (see below). An efficient reinforcement, however, was achieved in the networks with the continuous inorganic phase where a percolation of the silica/SSQO structure occurs [A39]. This is the case

of the ASO-networks containing a high TEOS amount and the EC-networks with a high EC excess.

The networks from ASO behave as particulate composites. Their mechanical properties are well described by crosslinking density determined by the Flory-Erman theory and including the inorganic filler hydrodynamic effect according to the Halpin-Tsai-Lewis-Nielsen particulate composite model. The bicontinuous morphology proved in the ASO-TEOS networks and EC networks with EC excess was quantitatively characterized by the extent of the continuity of the inorganic phase.

The *interphase interaction* in the O-I block copolymer networks is well defined but relatively weak. The SSQO domains are covalently bound and located only at the chain end. As a result, due to a sharp microphase separation, there is only a thin interphase layer involving the surface of the SSQO junction domain and a small terminal part of the immobilized bonded oligomer chain. The middle part of the chain remains free of restrictions. In addition to the covalent bonding there is a weaker H-bond interaction between silanol groups of the SSQO structure and ether grouping $-CH(CH_3)-OCH_2-$ of the poly(oxypropylene) chain of the organic matrix. Therefore, an internal SSQO structure (content of SiOH) controlled by the reaction conditions (acid catalysis, high content of water) is crucial for the interphase interaction [A39].

Epoxy networks with inorganic nanobuilding blocks

The rubbery epoxy networks based on DGEBA-poly(oxypropylene)diamines (mainly D2000) were used as an organic matrix and the POSS units as the well defined nanobuilding block. We have investigated three basic types of the epoxy-POSS networks in the papers [A41, A42, A46]

- networks with POSS covalently attached as pendant units
- networks with POSS as crosslink units
- networks with physically admixed POSS without a covalent bonding

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The networks with covalently bound POSS were prepared by using POSS monomers containing epoxy or amino functionalities (see Fig.1). The POSS with one epoxy (POSS,E1) or bifunctional amino group (POSS,A2) were incorporated in the epoxy network as pendant units, while the POSS with more functional epoxy groups (POSS,E_n) formed the polyfunctional crosslink of the hybrid network. The POSS without the reactive organic functionality was applied for preparation of physical mixtures of POSS and the epoxy system.
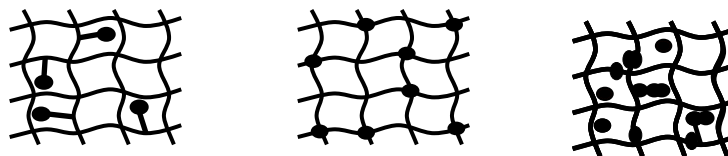

Figure 4   O-I networks with POSS as pendant unit, as network junctions and physically admixed POSS

The POSS units aggregate within the epoxy matrix to form the O-I nanostructured network. In order to control the POSS aggregation, which is a key to control the overall hybrid network structure and morphology, we have taken into account the following aspects:

  POSS topology in the network, i.e. POSS as a pendant unit   or as a network crosslink,

  POSS organic substituents affecting miscibility with an organic matrix,

  covalent bonding to the epoxy matrix,

  polymerization procedure of the network synthesis.

Epoxy networks with pendant POSS

Structure and morphology of the hybrid network is determined mainly by the type of POSS substituents governing compatibility with the organic matrix. The series of POSS monomers POSS,E1 and POSS,A2 containing octyl, butyl, phenyl and cyclopentyl substituents show increasing tendency to microphase separation and aggregation in the epoxy system. The hybrid networks with both amorphous or crystalline

POSS domains are formed. Crystallinity of the POSS monomers is restricted but not fully suppressed during polymerization and incorporation in the network. However, due to significant steric restrictions by bonding to the network chain the structure of the crystalline POSS domains in some cases is modified with respect to the monomer crystallizing without any hindrance [A41]. In addition to the thermodynamic factors also the kinetic effect contributes to the structure and phase evolution during the hybrid network formation due to a relatively low reactivity of the POSS functionalities [A46]. As a result, the distribution of POSS in the network is inhomogeneous.

Two step synthesis procedures was applied to improve POSS dispersion in the network and to homogenize the system. The approach (modified procedure by Liu et al.[34]) consisted in the prereaction of the amino functional monomer, POSS,A2, with DGEBA to form the epoxy-terminated adduct DGEBA-POSS,A2-DGEBA showing a better miscibility with the epoxy system.

Mechanical properties of the epoxy-POSS network, followed in the paper [A42] depend on the type of substituents of the pendant POSS governing the nanocomposite morphology. The POSS crystalline domains in the networks with POSS,E1,$_{Ph}$ or POSS,E1,$_{Et}$ (phenyl or ethyl substituents) act as polyfunctional POSS clusters and create strong physical crosslinks (Figure 5). These crystalline junctions are responsible for the reinforcement of the epoxy network. We have determined that POSS-POSS interaction and formation of physical crosslinks dominate the properties. On the contrary, the anchoring effect [28] of the large POSS mass on the chain mobility was shown to be of low importance.

Figure 5 Physical crosslinks in the epoxy-POSS networks

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Supramolecular ordering

The special type of the epoxy networks with pendant POSS were prepared by using the diepoxide monomer POSS$_{DGEBA}$, (i.e. POSS modified DGEBA) described in [A41]. During formation of the network POSS$_{DGEBA}$-D2000 a microphase separation takes place followed by ordering of the POSS crystalline domains in the epoxy network. The structure model of the hybrid network based on SAXS analysis consists of the lamellar ordering of the POSS crystal domains separated by the extended D2000 chains. The POSS crystalline layers bring about a reinforcement of the polymer network due to a physical crosslinking. The rubbery modulus of the network POSS$_{DGEBA}$-D2000 is higher by 1.5 order of the magnitude with respect to the reference DGEBA-D2000 network. The network structure is temperature dependent. At the critical temperature (T_C=120° C), the order-disorder transition occurs consisting in disordering of the POSS lamellar domains, which manifests itself by a steep drop-off modulus.

Epoxy networks with POSS in junctions

The POSS units localized in network junctions are well dispersed in the epoxy matrix in contrast to the POSS pendant on the chain in agreement with literature. We have followed in [A41] evolution of the phase structure during polymerization and determined conditions governing the POSS dispersion. It was found that increase in functionality of the epoxy functional POSS monomers (POSS,En) leads to a decrease in extent of aggregation.

The phase structure evolution during the network build-up is determined by competition between phase separation of the components and compatibilizing grafting reaction. The initial inhomogeneous mixture contains POSS aggregates. During polymerization the aggregates are gradually broken and POSS polyfunctional units become dispersed in the oligomeric amine forming network junctions. Formation of small chemical clusters, however, prevents a perfect molecular POSS dispersion [A46]. Finally, the ordered structure is developed with regularly arranged POSS crosslinks domains separated by D2000 chains.

The rubbery modulus of the hybrid networks increases with increasing functionality of the POSS monomer, i.e. with enhancing

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crosslinking density. The multiepoxy-POSS units, used in our system, contain hexyl substituents and act in the network as „soft" junctions. The network chains mobility is less restricted than by stiff DGEBA species in the reference DGEBA-D2000 network. In addition, the voluminous POSS unit acts as a plasticizer. Therefore, T_g of these hybrid networks with POSS junctions is lowered.

Thermal stability

The thermal stability and mainly thermal oxidation resistance of the epoxy networks was found in [A42] to increase by incorporation of POSS as pendant units. The temperature at which 5% loss of mass occurs, is increased by 20-60°C in the networks with phenyl- and cyclopentyl-substituted POSS. The networks with the strong POSS-chain interaction show the highest thermal stability, because due to this interaction the organic chain is shielded by an inorganic layer.

Responsive polymer networks

We have studied the responsive polymer networks sensitive to light [A1,A2] or to temperature [A44, A45].
 The *photosensitive polymer networks* show a photomechanical conversion as a result of a reversible change of polymer conformation after irradiation induced by photoisomerization of light-sensitive moieties bound to polymer. We have prepared the photochromic polymer networks based on the copolymer of maleic anhydride with styrene (PMAH-STY), polybutylacrylate (PBA) and poly(hydroxyethyl methacrylate) containing photochromic azo groups in side chains or in crosslinks [A1,A2]. The photochrome p-aminoazobenzene (AAB) undergoes a trans-cis photoisomerization upon irradiation (λ=365 nm) followed by a slow thermal back isomerization cis-trans. If the photochrome is covalently attached to the polymer, a change in its configuration and intramolecular interactions affect the chain conformation. The linear photochromic polymer P(MAH-STY-AAB) showed a contraction of the polymer chain reflected in a reversible decrease in reduced viscosity in solution by ~ 30% after irradiation. Radiation induces a very strong dipole moment in the azo bond and these dipoles become mutually oriented and attract each other so that the

more coiled conformations are preferred. Irradiation of crosslinked polymers, both swollen gels and dry elastic networks, containing photosensitive groups induces photomechanical effects. Dry elastic copolymer P(BA-methacryloylamidoazobenzene) crosslinked with ethylene- dimethacrylate exhibits the photoinduced contraction of the sample by 1%. We have determined also the effect of temperature rise in the sample as a result of irradiation contributing to the photo-effect.

The *O-I thermosensitive hydrogels* were prepared by modification of poly(N-isopropylacrylamide) (PNIPA)-based hydrogels with an inorganic phase generated in situ by the sol-gel process. Two types of the hybrid gels were synthesized [A44]: (a) PNIPA-bisacrylamide gel containing dispersed silica domains formed by the hydrolytic condensation of tetramethoxysilane and (b) the PNIPA hydrogel crosslinked through the covalently bonded SSQO domains. The latter gel was prepared by copolymerization of NIPA with [3-(methacryloyloxy)propyl]trimethoxysilane followed by the hydrolytic condensation of the pendant methoxysilyl groups to form SSQO junctions.

The PNIPA-based hydrogels are well known to exhibit the volume transition at T=32° C corresponding to LCST. The problems to be solved in these gels are related to poor mechanical properties and slow swelling-deswelling process. The synthesized heterogeneous O-I hydrogels show both acceleration of the swelling-deswelling kinetics and improvement of the mechanical properties, i.e. elastic modulus. The two-step polymerization technique was applied for preparation of superporous O-I hydrogels with the continuous porous structure exhibiting extremely fast response to the temperature change [A45]. This technique consists in polymerization below LCST in the first step up to the moment close to the gel point of the system, followed by polymerization below the freezing point of the mixture.

Conclusions

The study of polymer networks described in this work involves determination of the chemistry and reaction mechanisms of curing of the epoxide systems, description and interpretation of evolution of the polymer structure and formation of polymer networks, as well as evolution of the phase structure and build-up of the O-I networks. The results of our investigation contributed to general understanding of the polymer network formation. Determination of the relationships, network formation - structure/morphology - properties, makes it possible to optimize the system and synthesis procedure in order to prepare the tailor made material. Application of the theory of branching processes in particular complex network systems enabled prediction of the structure and final properties.

We have revealed approaches how to control structure and morphology of the hybrid O-I polymer networks, which is crucial aspect in synthesis of the nanocomposite materials. The O-I networks with in situ generated inorganic structures or well defined POSS nanobuilding blocks prepared by controlling the strength of the interface interaction show broad range of morphologies and mechanical properties. We have developed the new O-I material based on the epoxy hybrid network displaying a significant improvement of mechanical properties (modulus) and thermal stability. Moreover, special types of the polymer networks with photo- and thermo-responsive properties were synthesized.

References

Literature

1. C.A. May, Epoxy Resins Chemistry and Technology, M. Dekker, New York 1988
2. K. Dušek, Adv. Polym. Sci. 1, 78 (1986)
3. S. Luňák, K. Dušek, J.Polym.Sci. Polym. Symp. 53, 45 (1975)
4. R. Morgan, Adv. Polym.Sci. 72, 1 (1985)
5. K. Dušek, M. Ilavský, S. Luňák, J.Polym.Sci.Polym. Symp. 53,29 (1975)

6. R.F. Fischer, J. Polym. Sci. 44,155 (1960)

7. Y. Tanaka, H. Kakiuchi, J. Appl. Polym. Sci. 7, 1063 (1963)

8. Y. Tanaka, H. Kakiuchi, J. J. Macromol. Chem. 1, 307 (1966)

9. L. Shechter, J. Wynstra, R.J. Kurkjy, Ind. Eng. Chem. 48, 94 (1956)

10. J.P. Pascault, H. Sautereau, J. Verdu, R.J.J. Williams, Thermoseting Polymers, M. Dekker, New York 2002

11. K.Dušek, M. Dušková-Smrčková, Polymer Networks, Macromolecular Engineering 3, 1687 (2007)

12. Ch.Y-M.Tung, P.J. Dynes, J. Appl. Polym. Sci. 27, 659 (1982)

13. F. Chambon, H. Winter, Polym. Bul.l. 13, 499 (1985)

14. W.H. Stockmayer, *J.Polym.Sci.* 9,69 (1952)

15. R.F.T. Stepto, D.J.R. Taylor, in Cyclic Molecules, J.A. Semlyen, ed. Kluwer Academic Publishers, Dordrecht, 2000

16. E.J. Goethals, Makromol. Chem. Macromol. Symp. 42{43, 51 (1991)

17. M. Gordon, Proc.Roy.Soc. London, Ser. A 268, 240 (1962)

18. K. Dušek, Macromolecules 17, 716 (1984)

19. C.W. Macosko, D.R. Miller, Macromolecules 9, 199 (1976)

20. K. Dušek, Polym. Bull. 1, 523 (1979)

21. D. Stauffer, A. Coniglio, M. Adam, Adv. Polym. Sci. 44, 103 (1980)

22. J.E. Mark, Polym. Eng. Sci. 36, 2905 (1996)

23. J.Y. Wen, G.L. Wilkes, Chem. Mater. 8, 1667 (1996)

24. C.J. Brinker, G.W. Scherer, in Sol-Gel Science, Academic Press, New York 1989

25. A.R. Bassindale, T.R. Gentle, J. Mater. Chem. 3, 1319 (1993)

26. J.D. Lichtenhan, N.Q. Vu, J.A. Carter, J.W. Gilman, F.J. Feher, Macromolecules 26, 2141 (1993)

27. J.D. Lichtenhan, T.S. Haddad, J.J. Schwab, M.J. Carr, K.P. Chaffee, P.T. Mather, Polym. Prepr. 39(1), 489 (1998)

28. R.K. Bhardawaj, R.J. Berry, B.L. Farmer, Polymer 41, 7209 (2000)

29. L.E. Nielsen, R.F. Landel, in Mechanical Properties of Polymers and Composites, New York, M. Dekker,1994

30. P.E. Tomlins, B.E. Read, Plast. Rubber Compos. 16, 17 (1991)

31. J. Kolařík, Eur. Polym. J. 34, 585 (1998)

32. W.E.A. Davies, J. Phys. D4, 1176 (1971)

33. D. Staufer , in Introduction to percolation theory. Taylor and Francis, Philadelphia, 1985

34. H.Z. Liu, J. Polym. Sci., Part A, Polym. Chem. 44, 1869 (2006)

Author's papers relevant to the Thesis

A1. L. Matějka, K.Dušek, M.Ilavský : The thermal effect in the photomechanical conversion of a photochromic polymer
  Polymer Bulletin 1, 659-664 (1979)

A2. L. Matějka, M.Ilavský, K.Dušek, O.Wichterle : Photomechanical effects in crosslinked photochromic polymers
  Polymer 22, 1511-1515 (1981)

A3. L.Matějka, K.Dušek : Formation of polyurethane networks studied by the gel point method
  Polymer Bulletin 3, 489-495 (1980)

A4. L. Matějka, S.Pokorný, K. Dušek: Network formation involving epoxide and carboxyl groups. Course of the model reaction monoepoxide-monocarbonic acid
  Polymer Bulletin 7, 123-128 (1982)

A5. L. Matějka, J.Lovy, S.Pokorný, K.Bouchal, K. Dušek: Curing epoxy resins with anhydrides. Model reactions and reaction mechanism
  J.Polym.Sci.,Polym.Chem.Ed. 21, 2873-2885 (1983)

A6. L.Matějka, C.Houtman, C.W.Macosko : Polymerization of dicyclopentadiene - a new reaction injection molding system
  J.Appl.Polym.Sci. 30, 2787-2803 (1985)

A7. L.Matějka, S.Pokorný, K.Dušek : Acid curing of epoxies. Comparison of polymerization of the systems diepoxide - dicarboxylic acid and monoepoxide - cyclic anhydride
  Makromolekulare Chemie 186, 2025-2036 (1985)

A8. D.Doskočilová, L.Matějka, S.Pokorný, M.Březina, J.Štokr, I.Dobáš, K.Dušek : Curing of epoxy resins: Configurational structure and reactivity of stereoisomers in the model reaction of diglycidylaniline with N-methylaniline
  Polymer Bulletin 14, 123-129 (1985)

A9. L.Matějka, K.Dušek, I.Dobáš : Curing of epoxy resins with amines. Gelation of polyepoxides derived from diglycidyl aniline
Polymer Bulletin 14, 309-315 (1985)

A10. L.Matějka, K.Dušek : Specific features of the kinetics of addition esterification of epoxide with the carboxyl group
Polymer Bulletin 15, 215-221 (1986)

A11. L.Matějka, M.Tkaczyk, S.Pokorný, K.Dušek : Cyclization in the reaction between diglycidylaniline and amine
Polymer Bulletin 15, 389-396 (1986)

A12. K.Dušek, M.Ilavský, Š.Štokrová, L.Matějka, S.Luňák : Formation and structure of networks from poly(oxypropylene) polyamines and diglycidyl ether of Bisphenol A. II. Reactivity of aminogroups, gelation, sol fraction and equilibrium modulus
in : Crosslinked Epoxies (B.Sedláček, J.Kahovec,Eds.) Walter de Gruyter Publ., West Berlin 1987, pp.279-289

A13. L.Matějka, K.Dušek : Nework formation in the curing of epoxy resins : A comparison of the curing of Bisphenol A diglycidyl ether and polyepoxides based on N,N-diglycidylaniline
in : Crosslinked Epoxies (B.Sedláček, J.Kahovec,Eds.) Walter de Gruyter Publ., West Berlin 1987, pp.231-239

A14. L.Matějka, S.Pokorný, K.Dušek : Mechanism and kinetics of the reaction between diglycidylaniline and aromatic amines
in : Crosslinked Epoxies (B.Sedláček, J.Kahovec,Eds.) Walter de Gruyter Publ., West Berlin 1987, pp.241-250

A15. D.Reyx, B.Costes, L.Matějka, K.Dušek : Spectroscopic characterization of 1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane (8C ring compound) formed in N,N-diglycidylaniline/aniline systems
Polymer Bulletin 19, 269-274 (1988)

A16. Matějka, K.Dušek : The mechanism of curing of epoxides based on diglycidyl- amine with aromatic amines. I. Reaction of diglycidylaniline with secondary amines
Macromolecules 22, 2902-2910 (1989)

A17. Matějka, K.Dušek : The mechanism of curing of epoxides based on diglycidyl- amine with aromatic amines.II. Reaction of diglycidylaniline with aniline
Macromolecules 22, 2911-2917 (1989)

A18. G.Zeppenfeld, L.Matějka, P.Špacek, P.Schmidt, K.Dušek : Curing of epoxides. Reaction of dicyandiamide with phenylglycidyl ether
Angewandte Makromolekulare Chemie 172, 185-194 (1989)

A19. A.Vazquez, L.Matějka, P.Špaček, K.Dušek : Polymerization of epoxides in the presence of tertiary aminoalcohols
J.Polym.Sci.,Polym.Chem.Ed. 28, 2305-2319 (1990)

A20. L.Matějka: Reaction mechanism and   structure of amine cured epoxy resins
Proc.Annu. Conf. on Crosslinked Polymers, Luzern 1990, pp.123-133

A21. L.Matějka, P. Špaček, K. Dušek: Cyclization in amine-cured N,N-iglycidylaniline   epoxy resins
Polymer 32,3190-3194 (1991)

A22. L.Matějka, K. Dušek: Influence of the reaction mechanism on the network
formation   of amine-cured N,N-diglycidylamine   epoxy resins
Polymer 32,3195-3200 (1991)

A23. L.Matějka: Rheology of epoxy networks near the gel point
Polymer Bulletin 26,109-116 (1991)

A24. L.Matějka, Š.Podzimek, W.J.Simonsick Jr.,P. Špaček,K. Dušek: Model reactions of amine curing of glycidylamine epoxy resins. Homopolymerization of N-methyglycidylaniline
J.Polym.Sci., Polym.Chem.Ed. 30,2109 (1992)

A25. L.Matějka, P.Chabanne, L.Tighzert, J.P.Pascault: Cationic polymerization of diglycidylether of Bisphenol A
J.Polym.Sci.,Polym.Chem.Ed. 32,1447 (1994)

A26. L.Matějka, K. Dušek: Curing of diglycidylamine based epoxides with amines. Kinetic models and simulation of structure development
J.Polym.Sci.,Polym.Chem.Ed. 33,461-472 (1995)

A27. L.Matějka, Š.Podzimek, K. Dušek: Differences in structure growth in amine curing of diglycidylether of Bisphenol A and N,N-diglycidylaniline epoxy resins. Bifunctional models
J.Polym.Sci.,Polym.Chem.Ed. 33, 473-480 (1995)

A28. K. Dušek L.Matějka, P. Špaček, H.Winter : Network formation in the free-radical copolymerization of a bismaleimide and styrene
Polymer 37, 2233-2243 (1996)

A29. L.Matějka, K. Dušek, P.Chabanne, J.P.Pascault : Cationic polymerization of diglycidyl ether of Bisphenol A.2.Theory
J.Polym.Sci.A: Polym.Chem. 35, 651-663 (1997)

A30. L.Matějka, K. Dušek, P.Chabanne, J.P.Pascault : Cationic polymerization of diglycidyl ether of Bisphenol A. 3.Comparison of the theory with experiment
J.Polym.Sci.A: Polym.Chem. 35, 665-672 (1997)

A31. L.Matějka, K.Dušek, J.Pleštil, J.Kříž, F.Lednický : Formation and structure of the epoxy-silica hybrids
Polymer 40, 171-181 (1999)

A32. L.Matějka, J.Pleštil, K.Dušek: Structure evolution in epoxy-silica hybrids
J.Non-Cryst.Solids 226, 114-121 (1998)

37

A33. L.Matějka, O.Dukh, J.Kolařík: Reinforcement of crosslinked rubbery epoxies by in-situ formed silica
Polymer 41, 1449-1459 (2000)

A34. L.Matějka, O.Dukh, J.Brus, W.J.Simonsick, B.Meissner: Cage-like structure formation during sol-gel polymerization of glycidyloxypropyl-trimethoxysilane
J.Non-Cryst.Solids 270 (1-3), 34-47 (2000)

A35. L.Matějka : Amine cured epoxide networks – Formation, structure and properties
Macromolecules 33, 3611-3619 (2000)

A36. L.Matějka, O.Dukh : Organic-inorganic hybrid networks
Macromol.Symp. 171, 181-188 (2001)

A37. L.Matějka, O.Dukh, D.Hlavatá, B.Meissner, J.Brus : Cyclization and self- organization in polymerization of trialkoxysilanes
Macromolecules 34, 6904-6914 (2001)

A38. L.Matějka, O.Dukh, B.Meissner, D.Hlavatá, J.Brus, A.Strachota : Block-copolymer organic-inorganic networks. Formation and structure ordering
Macromolecules 36 (21), 7977-7985 (2003)

A39. L.Matějka, O.Dukh, H.Kamišová, D.Hlavatá, M.Špírková, J.Brus : Block-copolymer organic-inorganic networks. Structure, morphology and thermomechanical properties
Polymer 45 (10), 3267-3276 (2004)

A40. M.Gonzalez, P. Kadlec, P.Štěpánek, A.Strachota, L.Matějka :Crosslinking of epoxy-polysiloxane system by reactive blending
Polymer 45, 5533-5541 (2004)

A41. L.Matějka, A.Strachota, J.Pleštil, P.Whelan, M.Steinhart, M.Šlouf: Epoxy networks reinforced with polyhedral oligomeric silsesquioxanes (POSS). Structure and morphology
Macromolecules 37 (25), 9449-9456 (2004)

A42.   A.Strachota, I.Kroutilová, J.Kovářová, L.Matějka : Epoxy
networks reinforced with polyhedral oligomeric silsesquioxanes
(POSS). Thermomechanical properties.
Macromolecules 37 (25), 9457-9464 (2004)

A43. I. Kroutilová, L. Matějka, A. Sikora, K. Souček, L. Staš : Curing of
epoxy systems at   sub-glass transition temperature
J.Appl.Polym.Sci. 99, 3669-3676 (2006)

A44. M. Lutecki , B. Strachotová, M. Uchman, J. Brus, J. Pleštil, L.
Matějka :   Thermosensitive PNIPA-based organic-inorganic
hydrogels
Polymer Journal 38 (6), 527-541 (2006)

A45. B. Strachotová, A. Strachota, M. Uchman, M. Šlouf, J. Brus, J.
Pleštil, L. Matějka : Super porous organic-inorganic poly(N-
isopropylacrylamide)-based hydrogel with a very fast temperature
response
Polymer 48, 1471-1482 (2007)

A46. A.Strachota, P. Whelan, J. Kříž, J. Brus, M. Urbanová, M. Šlouf,
L.Matějka
Formation of nanostructured epoxy networks containing polyhedral
oligomeric   silsesquioxane (POSS) blocks
Polymer 48(11), 3041-3058, (2007)

A47. L. Matějka
Epoxy-silica/silsesquioxane polymer nanocomposites
In: Hybrid Nanocomposites (L. Merhari, Ed.) Springer   Verlag, in
press

Summary

The thesis dealing with investigation of a broad range of polymer networks is divided into three parts : (1) Reaction mechanism and kinetics of the epoxy networks synthesis, (2) Polymer networks formation, structure and properties, and (3) Organic-inorganic networks. In addition, a short paragraph describes the special networks showing the photo- and thermoresponsive properties.

The chemistry and mechanism of the crosslinking reaction is crucial for a network formation. We have described *mechanism and kinetics of the reaction* of the epoxides with different curing agents, the most important being the curing with acid anhydrides, carboxylic acids and amines.

We have evaluated the influence of the reaction mechanism on the *process of network formation*. The results of our investigation contributed to general knowledge about formation, structure and properties of polymer networks. The main factors governing the network build-up and the resulting structure were determined. The effect of cyclization, unequal reactivity of functional groups or the type of crosslinking polymerization was revealed. The theory of branching processes was used to describe and predict the network formation.

The main part of the thesis deals with the study of the nanostructured *organic-inorganic (O-I) networks*. We have investigated and described two types of the O-I nanocomposites – (a) the systems with the inorganic "silica filler" in situ generated by the sol-gel process within the epoxy matrix, and (b) the networks containing well defined inorganic nanobuilding blocks, polyhedral oligomeric silsesquioxanes – POSS. We have found the approaches for an effective control of the structure and morphology of the hybrid systems and determined the effect of the interphase interaction. Finally, we have developed the new O-I material based on the epoxy hybrid network showing a significant reinforcement and an improvement of thermal stability.

Other author's papers

B1. L.Matějka, S.Nešpůrek, M.Kucharski, K.Dušek : A photosensitive polymer as recording material in holography
Polymer Bulletin 1, 167-170 (1978)

B2. L. Matějka, K.Dušek : Photochromic polymers : Photoinduced   conformational changes and effect of polymeric matrix on the isomerization of photochromes
Makromolekulare Chemie 182, 3223-3236 (1981)

B3. K. Dušek, S.Luňák, L. Matějka: Gelation in the curing of epoxy resins with anhydrides
Polymer Bulletin 7, 145-152 (1982)

B4. K. Dušek, M.Ilavský, L. Matějka: Statistical treatment of allophanate crosslinking in the formation of polyurethane networks
Polymer Bulletin 12, 33-40 (1984)

B6. K.Kajiwara, W.Burchard, K.Dušek, M.Kowalski, L.Matějka, D.Nerger, Y.Tuzar : Dynamic and static light scattering from critically branched polymer solutions
Makromolekulare Chemie 185, 2543-2552 (1984)

B7. K. Dušek, L. Matějka: Transesterification and gelation of polyhydroxyesters formed from diepoxides and dicarboxylic acids
in "Rubber-modified thermoset resins", Adv.Chem.Ser.208, ACS,   Washington, D.C., 1984, pp.15-26

B8. K.Dušek, L.Matějka : Amine curing of epoxy resins derived from N,N-diglycidylamines
Polym.Mater.Sci.Eng. 56, 356-360 (1987)

B9. K.Dušek, L.Matějka : Advances in network formation and   rheology during curing of epoxy resin systems including reactive liquid elastomers
Polym.Mater.Sci.Eng. 57, 765-769 (1987)

B10. K.Dušek, L.Matějka : Special features of network build-up in curing of polyepoxides based on N,N-diglycidylaniline   derivatives
in : Biological and Synthetic Polymer Networks, Elsevier   Publ., Amsterdam 1988, pp.335-344

B11. L.Matějka, L.Lochmann, P.Schmidt: An infrared study of interactions in the system sodium tert-butoxide - tetrahydrofuran
Collection Czech.Chem.Commun. 54, 308-315 (1989)

B12. K.Dušek, L.Matějka : Formation of epoxy networks, including   reactive liquid elastomers
Adv.Chem.Ser.222, ACS Washington, D.C. 1989, in : Rubber-Toughened Plastics , pp.303-318

B13. L.Matějka: Thermoreactive matrices (in Czech)
in : Polymeric composites (J.Kahovec, J.Pouchlý, Eds.), Inst.Macromol.Chem., Praha 1990 , pp.94-100

B14. K. Dušek, J.Šomvársky, M.Ilavský L.Matějka: Gelation and network formation by polyetherification of polyepoxides Initiated by hydroxyl groups:Theory
Computational Polymer Sci. 1,2,90 (1991)

B15. M. Špírková , L.Matějka, K. Dušek: Epoxy-silica hybrid networks
In: "Silicon-Containing Polymers", (R.G.Jones, Ed.), Royal Society of Chemistry, Cambridge, Canterbury, 1995, pp. 51-56

B16. L.Matějka, J.Pleštil : Structure development during sol-gel process in organic-silica networks
Macromol.Symp. 122, 191-196 (1997)

B17. L.Matějka, K.Dušek, J.Noga : Formation, structure and mechanical properties of the organic-silica hybrid networks
Wiley Polymer Networks Goup Review(W.J.Nijs, K.de Nijenhuis,Eds), Ser.Vol.1,1997, pp. 301-311

B18. N.C.Beck Tan, B.J.Bauer, J.Pleštil, J.D.Barnes, D.Liu, L.Matějka, K.Dušek, W.L.Wu : Network structure of bimodal epoxies – a small angle X-ray scattering study
Polymer 40, 4603-4614 (1999)

B19. L.Matějka : Silica structures formed by sol-gel process as modifiers of epoxy networks
Polymer Preprints 39, 573-574 (1998)

B20. M.Špírková, L.Matějka, D.Hlavatá, B.Meissner : Polybutadiene-based polyurethanes with controlled properties : Preparation and characterizaton
J.Appl.Polym.Sci. 77 (2), 381-389 (2000)

B21. B.Meissner, L.Matějka : Description of the tensile stress-strain behavior of filler reinforced rubberlike networks using a Langevin theory-based approach. Part I.
Polymer 41, 7749-7760 (2000)

B22. L.Matějka, O.Dukh, D.Hlavatá, J.Brus, W.J.Simonsick,Jr. : Sol-gel polymerization of alkyl(trialkoxy)silanes – formation of cage-like silsesquioxane structures
Polymer Preprints 41(1), 502 (2000)

B23. L.Matějka: In-situ formed siloxane-silica filler for rubbery organic networks
in "Silicones and Silicone-Modified Materials",(ACS, Washington,DC, eds.S.J.Clarson, J.J.Fitzzgerald, M.J.Owen, S.S.Smith) , ACS Symp.Ser.729, 2000, pp.485-502

B24. B.Meissner, L.Matějka : Description of the tensile stress-strain behavior of filler reinforced rubberlike networks using a Langevin theory-based approach. Part II.
Polymer 42 (3), 1143-1156 (2001)

B25. B.Meissner, L.Matějka : Comparison of recent rubber-elasticity theories with biaxial
stress-strain data: the slip-link theory of Edwards and Vilgis
Polymer 43 (13), 3803-3809 (2002)

B26. A.Strachota, G.Tishchenko, L.Matějka, M.Bleha : Chitosan – oligo(silsesquioxane)
blend membranes : Preparation, morphology, and diffusion permeability
Journal of Inorganic and Organometallic Polymers 11 (3), 165-182 (2001)

B27. L.Matějka : Structure characterization of organic-inorganic nanocomposites formed
by the sol-gel polycondensation
MRS Symp.Proc. 726, 57-63 (2002)

B28. M. Špírková, J. Brus, D. Hlavatá, H. Kamišová, L. Matějka, A. Strachota :
Preparation and characterization of hybrid organic-inorganic coatings and films
Surf. Coat. International B 86, B3,187 (2003)

B29. M.Špírková, J.Brus, D.Hlavatá,H.Kamišová, L.Matějka, A.Strachota:
Preparation and characterization of hybrid organic-inorganic epoxide-based
free standing films and coating films prepared by sol–gel process
J. Appl. Polym. Sci. 92 (2), 937-950 (2004)

B30. B.Meissner , L.Matějka : A Langevin-elasticity-theory-based constitutive equation
for rubberlike networks and its comparison with biaxial stress-strain data. Part I.
Polymer 44, 4599-4610 (2003)

B31. B.Meissner , L.Matějka .: Langevin-elasticity-theory-based description of the tensile
properties of double network rubbers.
Polymer 44, 4611-4617 (2003)

B32. B. Meissner , L.Matějka : Analysis of the biaxial stress-strain behavior of
poly(dimethylsiloxane) networks from the viewpoint of the slip-link model of rubber
elasticity
J Polym Sci, Part B, Polym. Phys 42 (12), 2318-2328 (2004)

B33. B. Meissner, L.Matějka : A Langevin-elasticity-theory-based constitutive equation
for rubberlike networks and its comparison with biaxial stress-strain data. Part II.
Polymer 45, 7247-7260 (2004)

B34. M.Špírková, J.Brus, L.Matějka : Epoxy-based organic-inorganic nanocomposite
coatings and films prepared by sol-gel process
Scientific Israel-Technological Advantages 6 (3-4), 7 –15 (2004)

B35. B.Meissner, L.Matějka : Kinetic limitations in the formation of end-linked elastomer
networks
Polymer 46, 10618-10625 (2005)

B36. J.Vraštil, L.Matějka, V.Špaček, M.Večeřa, L.Prokůpek : Organization in sol-gel polymerization of methacrylate co-oligomers containing trimethoxysilylpropyl-methacrylate
Polymer 46(25), 11232-11240 (2005)

B37. E. Martinez-Ferrero, F. Ribot, L. Rozes, C. Sanchez, and L. Matějka : Functionalized tin clusters as nanobuilding blocks for hybrid materials
Progress inn Solid State Chemistry 33, 89-97 (2005)

B38. D.P.Fasce, R.J.J.Williams, L.Matějka, J.Pleštil, J.Brus, B.Serrano, J.C. Cabanelas, J. Baselga: Photoluminiscence of bridged silsesquioxanes containing urea or urethane groups with nanostructures generated by the competition between the rates of self-assembly of organic domains and the inorganic polycondensation
Macromolecules 39 (11), 3794-3801 (2006)

B39. B. Meissner, L. Matějka : A structure-based constitutive equation for filler-reinforced rubber-like networks and for the description of the Mullins effect
Polymer 47, 7997-8012 (2006)

B40. H.E. Romeo, M. A. Fanovich, R. J. J. Williams, L. Matějka, J.Pleštil, J. Brus: Self-Assembly of a Bridged Silsesquioxane Containing a Pendant Hydrophobic Chain in the Organic Bridge
Macromolecules 40, 1435-1443 (2007)

B41. H.E. Romeo, M. A. Fanovich, R. J. J. Williams, L. Matějka, J.Pleštil, J. Brus: Bridged silsesquioxanes with organic domains self-assembled as functionalized molecular channels
Macromol. Chem. Phys. 208, 1202 (2007)

B42. M.L.Gómez, D.P. Fasce, R.J.J. Williams, C.M. Previtali, L.Matějka, J. Pleštil, J. Brus : Tuning the photoluminescence of silsesquioxanes with short substituted urea bridges
Macromol. Chem. Phys. 2008

B43. B. Meissner, L. Matějka: Constitutive equation describing the biaxial stress-strain behavior of poly(dimethylsiloxane) networks reinforced with silica generated in situ.
European Polymer Journal, 44(7), 1940-1948 (2008)

B44. B. Meissner, L. Matějka: Biaxial stress-strain behavior of chemical and physical gels of poly(vinyl alcohol)
Polymer 49, 2560 (2008)

B45. I.A. Zucchi, C.E. Hoppe, M.J. Galante, R.J.J. Williams, M.A. López-Quintela, L. Matějka, M. Šlouf, J. Pleštil : Self-assembly of gold nanoparticles as colloidal crystals induced by polymerization of amphiphilic monomers
Macromolecules 41 (13), 4895-4903, (2008)

44

B46. Z. Špitálsky, A. Kromka, L. Matějka, P. Černoch, , J. Kovářová, J. Kotek, M. Šlouf :
      Effect of nanodiamond particles on properties of epoxy composites
      Advanced Composites Letters 17 (1), 29-34 (2008)

B47. Z. Špitálsky, L. Matějka, M. Šlouf, J. Stejskal, J. Kovářová, J. Zemek, J. Kotek:
      Modification of carbon nanotubes and its effect on properties of carbon
      nanotube/epoxy nanocomposites
      Polymer Composites 2008, DOI 10.1002/pc

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