Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates

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ABSTRACT

Epoxy resins are very important and widely used thermosetting polymers that find many practical applications. Very often their properties can be effectively modified by an addition of reactive silanes, polysiloxanes, silsesquioxanes, silica, montmorillonite, and other fillers. This review considers the literature concerning: (a) synthesis of carbofunctional silanes (CFS), polysiloxanes (CFPS) and polyhedral silsesquioxanes (POSS); (b) properties of neat epoxy resins and their composites and nanocomposites, obtained by modifications with reactive silanes, silicon containing monomers and polymers, and silica based fillers, enabling improvement of their mechanical properties, thermal and flame resistance as well as providing corrosion and antimicrobial protection.

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Contents

1. Introduction

Considerable interest has developed in applications of reactive functional silanes and polysiloxanes, mostly involving compounds with carbofunctional groups. They are used in many fields of science, and especially in materials science and a chemical technology. This interest widens the range of their numerous applications [1]. Moreover, silica, in situ generated nanosilica (by a sol–gel process), silane modified silicas, other fillers and nanofillers have often been used for modifications of different polymers and polymeric materials.

2. Reactive silanes and siloxanes in silicon chemistry

In organosilicon chemistry most important are following functional groups: $\equiv$Si—Cl, $\equiv$Si—OR, $\equiv$SiOCOR (R—usually alkyl group), $\equiv$Si—H, and $\equiv$Si—CH=CH$_2$. Functional organic silanes include: chlorosilanes, alkoxysilanes, and acetoxysilanes, hydrosilanes, and different functional and carbofunctional silanes [2–5]. These silyl functional groups are present both in organosilicon monomers (e.g., dimethyldichlorosilane, methyltriethoxysilane, methyltriacetoxysilane, etc.) and polymers, and can be grafted on

silica, silicates, and other inorganic fillers as well. Silicon tetrachloride $SiCl_4$, trichlorosilane $HSiCl_3$, dichlorosilane H_2SiCl_2 are the most often used inorganic chlorosilanes. Chlorosilanes easily react with alcohols, metal alkoxides, and carboxylic acids giving appropriate alkoxysilanes or acyloxysilanes, respectively. Esters of silicic acid: tetraethoxysilane $Si(OEt)_4$ (TEOS), tetramethoxysilane $Si(OMe)_4$ (TMOS), and tetraacetoxysilane $Si(OAc)_4$ are very useful silicon monomers as well.

The "hydrolytic polycondensation" of chlorosilane monomers of different functionality is one of main routs to linear and cyclic functional siloxanes and polysiloxanes (silicones). This multistep condensation process includes consecutive and parallel hydrolysis and condensation elementary reactions:

$$\equiv Si-Cl + H_2O \rightarrow \equiv Si-OH + HCl \qquad (1)$$

$$\equiv Si-Cl + HO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + HCl \qquad (2)$$

$$\equiv Si-OH + HO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + H_2O \qquad (3)$$
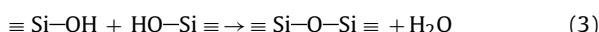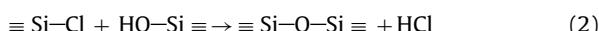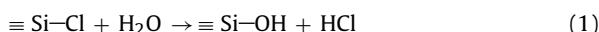
Linear oligo- and polysiloxanes having different functional groups (most often silanol, chlorosilyl, hydrosilyl, vinyl, and allyl groups) and cyclic siloxanes find many applications in further syntheses.

2.1. Carbofunctional silanes (CFS)

The carbofunctional silanes (CFS) are compounds with the general formula $X_nSi(R'Y)_{4-n}$, where: X—a functional group sensitive to hydrolysis (Cl, OR, OCOR), Y—a functional group, e.g., Cl, NH_2, NR_2, OH, OCOR, NCO, CH_2=CH, SH, and R'—alkylene chain, usually built of three methylene groups [6–10]. CFS are usually called *silane coupling agents* (SCA), because of the presence of two functional groups X and Y. They are employed in miscellaneous practical applications, and are often used for modification of plastics properties. CFS form chemical bonds with inorganic materials as a result of reactions of functional groups X (that most often are alkoxy groups), while the functional groups Y may react with organic polymers. Commercially available are alkoxysilanes of a structure $(RO)_3Si(CH_2)_3Y$, most often with methoxy or ethoxy groups, and amine $-NH_2$, glycidyloxy $-O-CH_2-(CH-CH_2O)$ or methacryloxy $-O-CO-C(CH_3)=CH_2$ as organic functional Y groups, e.g., 3-(trimethoxysilyl)propyl methacrylate [11] and tetrakis-[(methacryloyloxy)ethoxy]silane (TMES) [12].

Numerous studies concerned silanes containing a single reactive functional group, such as 3-(trimethoxysilyl)propyl methacrylate (3-methacryloxypropyltrimethoxysilane) [10] or (3-glycidoxypropyl)trimethoxysilane (GPTMS) [13]. GPTMS is an often used SCA [14,15] that serves as a bridging unit. It forms interphase links through the hydrolysis and condensation reactions of alkoxysilane groups, and the simultaneous polymerization of epoxy group [16]. Far fewer syntheses of silanes having two, three or four reactive groups have been carried out [12,13,17,18].

Tetraacrylate, tetramethacrylate silanes and bis-acrylate-spiro-silane were readily synthesized in high yields (>95%) by alcoholysis of $SiCl_4$ in the
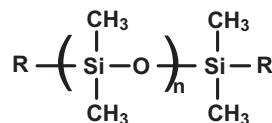
Fig. 1. The chemical structure of CFPS (R = hydroxyalkyl, chloroalkyl groups, aminoalkyl, vinyl, allyl, etc.) [1].

presence of a base [19]. Hydroxyalkyl functional (trialkoxy)silanes were synthesized by acidic hydrolysis of appropriate epoxy derivatives or by reaction of (isocyanatepropyl)triethoxysilane with (diethanol)amine (Scheme 1) [20]. Hydroxyalkyl terminated silanes with urethane moieties were prepared from ethylene carbonate and (3-aminopropyl)(ethoxy)dimethylsilane (a), (3-aminopropyl)(diethoxy)methylsilane (b) or (3-aminopropyl)(triethoxy)silane (c) (Scheme 2) [21].

Polycaprolactone functionalized with [(trialkoxysilane) propyl]urethane groups was synthesized from polycaprolactone-α,ω-diol and (isocyanatopropyl)triethoxysilane [22–24].

2.2. Carbofunctional polysiloxanes (CFPS)

Carbofunctional polydimethylsiloxanes (CFPS) have different functional alkylene groups on their chain ends (most often: hydroxypropyl, aminopropyl, glicydoxypropyl, or methacryloxypropyl groups), with the general structure shown in Fig. 1.

Carbofunctional polysiloxanes may also be terminated with olefins (e.g., vinyl or allyl groups) or with arylamine groups: $-C_6H_4NH_2$ [25].

CFPSs are frequently used for syntheses of hybrid silicone–organic copolymers and for the modification of many polymers and plastics to prepare numerous new polymeric materials with profitable properties [1]. Both CFS and CFPS are often applied to modifiy epoxy resins.

2.2.1. Syntheses of CFPS

Hydrosilylation is the fundamental reaction used to prepare carbofunctional polysiloxanes [2,26(a)]. CFPS end hydroxypropyl groups are products of hydrosilylation reactions of α,ω-dihydropolysiloxanes with allyl compounds [26(b)], e.g., allyloxytrimethylsilane and subsequent hydrolysis reaction of alkoxysilane terminal groups (Scheme 3) [27]. Starting α,ω-dihydrosiloxanes are synthesized via condensation reactions of polydimethylsiloxane-α,ω-diols with chloro(hydro)dimethylsilane.

Platinum Speier's and Karstedt's catalysts are most often applied, but they afford unsatisfactory yield and selectivity of products in the addition of allylamine to tetramethylcyclotetrasiloxane D_4^H (D^H = MeHSiO) [28]. Platinum oxide PtO_2 was found to be a very useful catalyst, resistant to "poisoning" by amine groups, giving the product with almost 100% yield and the very good selectivity, determined by a ratio of isomers γ/β = 93:7 [29].

Secondary (3-aminoalkyl) substituted telechelic polysiloxanes (Scheme 4) were prepared via reaction of poly(dimethylsiloxane-α,ω-diols) with a cyclic silazane [30,31]:
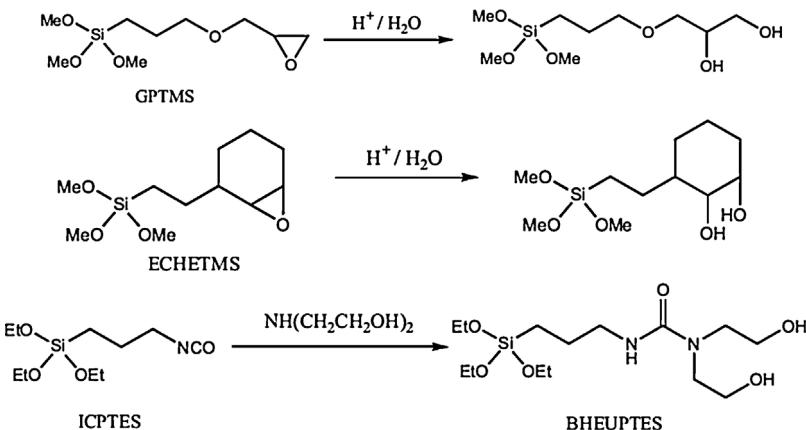
Scheme 1. A formation of hydroxyl functional (alkoxy)silanes. Reprinted (adapted) with permission from [20]. Copyright (2001) American Chemical Society.
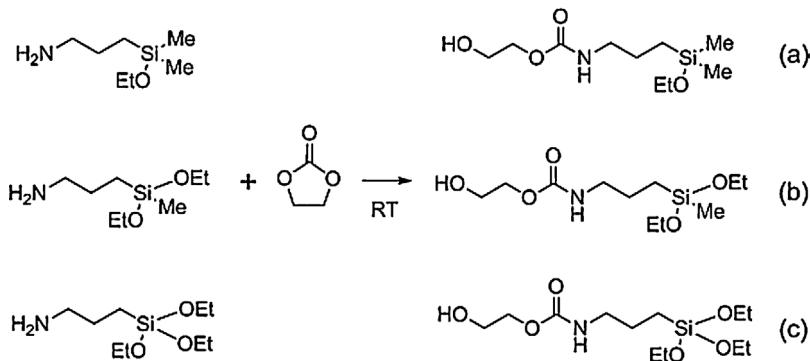
Scheme 2. A synthesis of hydroxylpropyl substituted urethane(alkoxy)silanes. Reprinted (adapted) with permission from [21]. Copyright© 2012, Springer Science + Business Media B.V.

HO-(Me$_2$SiO)$_n$-H   +   2 ClMe$_2$SiH $\xrightarrow{- 2HCl}$ HMe$_2$SiO-(Me$_2$SiO)$_n$-SiMe$_2$H

$\downarrow$ [Pt]   2 CH$_2$=CH-CH$_2$-OSiMe$_3$

Me$_3$SiO-CH$_2$CH$_2$CH$_2$-SiMe$_2$O-(Me$_2$SiO)$_n$-SiMe$_2$-CH$_2$CH$_2$CH$_2$-OSiMe$_3$

$\downarrow$ H$_2$O / H$^+$

HO-(CH$_2$)$_3$-SiMe$_2$O-(Me$_2$SiO)$_n$-SiMe$_2$-(CH$_2$)$_3$-OH
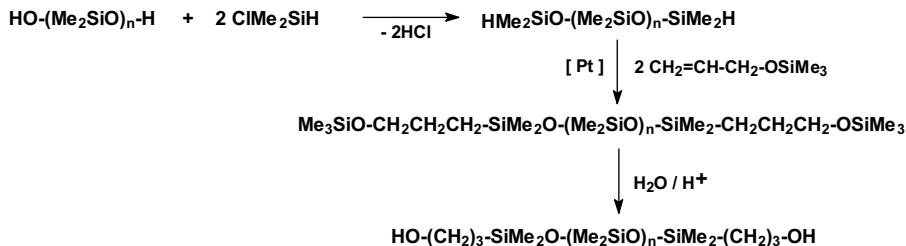
Scheme 3. The synthesis of polydimethylsiloxanes terminated with hydroxypropyl groups [1].

Few bis-aminodisiloxanes are commercially available, for example: 1,3-bis(3-amino-propyl)-1,1,3,3-tetra-methyldisiloxane, or the bis(aminoethylaminomethyl)-1,1,3,3-tetramethyl-disiloxane (Fig. 2) [32–35].

Syntheses of many other bis- and multi-substituted aminoalkyl disiloxanes have been described [33]. 1, 3-Bis(propylaminopropyl)-1,1,3,3-tetramethyldisiloxane (Scheme 5) was prepared by reaction of 1,3-bis
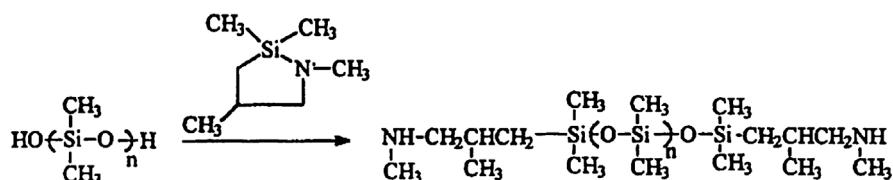
Scheme 4. Synthesis of a secondary amino-terminated PDMS.
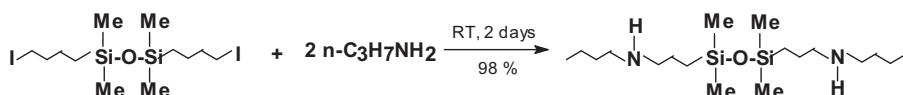
Scheme 5. The synthesis of 1,3-bis(propylaminopropyl)-1,1,3,3-tetramethyldisiloxane.
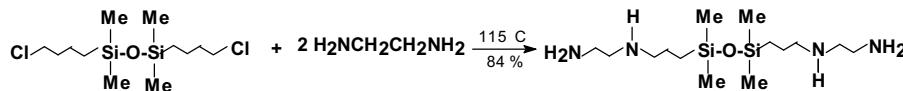
Scheme 6. Synthesis of 1,3-bis(3-[2-aminoethyl)aminopropyl]-1,1,3,3-tetramethyldisiloxane.
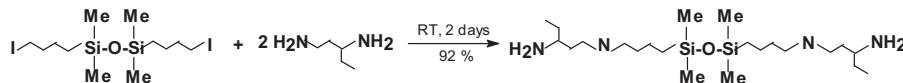
Scheme 7. The synthesis of 1,3-bis(3-(2-aminobutyl)aminopropyl)-1,1,3,3-tetramethyldisiloxane.
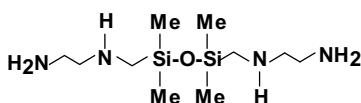
Fig. 2. The structure of bis(aminoethylaminomethyl)-1,1,3,3-tetramethyldisiloxane.

(3-iodopropyl)-1,1,3,3-tetramethyldisiloxane with *n*-propylamine:

1,3-Bis(3-[2-aminoethyl)aminopropyl]-1,1,3,3-tetramethyldisiloxane was synthesized in reaction of the 1,3-bis(chloropropyl)-1,1,3,3-tetramethyldisiloxane with an excess of ethylene diamine (Scheme 6) [33]:

A tetrafunctional hindered 1,3-bis(3-(2-aminobutyl) aminopropyl)-1,1,3,3-tetramethyldisiloxane was prepared via the reaction of 1,3-diaminopentane with 1,3-bis(3-iodopropyl)-1,1,3,3-tetramethyldisiloxane (Scheme 7) [33].

Hydrosilylation of tetramethyldisiloxane with allyl cyanide gave 1,3-bis(4-cyanobutyl)-1,1,3,3-tetramethyl-disiloxane, that was subsequently reduced with lithium aluminum hydride (LAH) to 1,3-bis(4-aminobutyl)-1,1,3,3-tetramethyldisiloxane (Scheme 8) [33].

1,3-Bis[4,4-di(aminomethyl)butyl]-1,1,3,3-tetramethyldisiloxane was synthesized by two step procedure (Scheme 9) [33].

A mixture of linear and cyclosiloxane oligomers containing 3-aminopropyl and (3-aminoethylamino)propyl substituents was prepared by a controlled hydrolytic

copolycondensation of (3-aminopropyl)(dietoxy)methyl-silane and [(3-aminoethylamino)propyl]-(dimethoxy) methylsilane [36]. These products were used as new generation polycationic supports of DNA ("*gene transfer reagents*").

The mixture of aminofunctional polysiloxanes was prepared via polycondensation reaction between aminoalkyl(alkoxy)silanes and polysiloxanes with sila-nol groups, that was catalyzed by carboxylate salt of aminoalkyl(alkoxy)silane. They are useful in the textile industry as fiber lubricants, in the personal care industry and they can also serve as ingredients of polishes or protective coatings [37].

Poly(3-aminopropyl, methyl)siloxane (PAMS) (Fig. 3) was synthesized by hydrolysis and condensation of (3-aminopropyl)(diethoxy)methylsilane at room temperature [38,39]. It contained 15 wt.% of cyclics. In comparison with other common amine hardeners poly(aminosiloxane) showed an enhanced reactivity against cycloaliphatic epoxy resins [40].

Ionic polymerization reactions of carbofunctional dis-iloxanes with cyclosiloxanes, most often with octamethyl-cyclotetrasiloxane (Me$_2$SiO)$_4$ (D$_4$) (Scheme 10), with acids or bases, are commonly applied methods for the prepara-tion of CFPS [41,42].

Poly(dimethyl)-*co*-(aminopropyl, methyl)siloxane oils, containing side aminopropyl groups, were obtained in this way by the equilibration of D$_4$ with (3-amino-propyl)methyldiethoxysilane and hexa-methyldisiloxane Me$_3$SiOSiMe$_3$ [34,43,44].
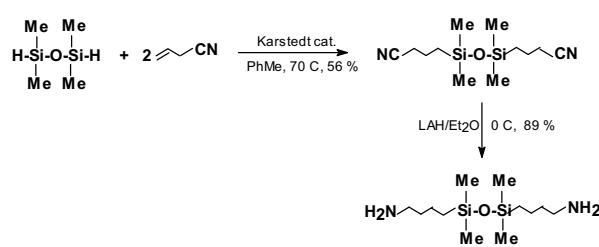
Scheme 8. The synthesis of 1,3-bis(4-aminobutyl)-1,1,3,3-tetramethyl-disiloxane.
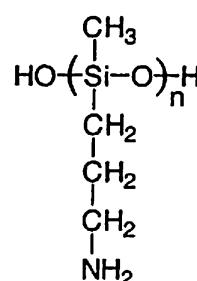
Fig. 3. The structure of PAMS.
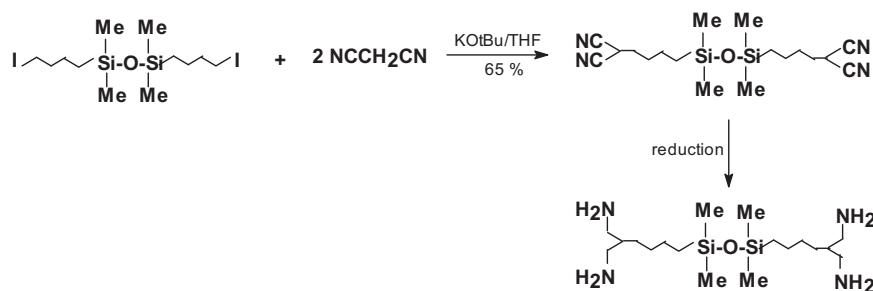
Scheme 9. The synthesis of 1,3-bis(4-aminobutyl)-1,1,3,3-tetramethyldisiloxane.
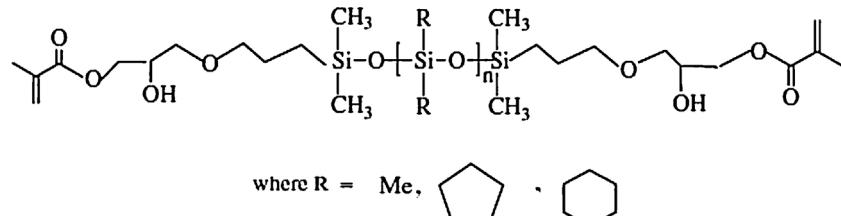
Fig. 4. The chemical structure of methacrylic functionalized siloxanes. Reprinted (adapted) with permission from [49]. Copyright 2010, Springer Science + Business Media B.V.
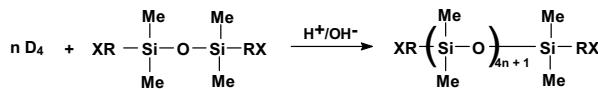
Scheme 10. The catalytic equilibriation of the carbofunctional disiloxanes with D_4 as a synthetic route to CFPS [1].

Aminofunctional polysiloxanes with different structures were obtained by the equilibriation of D_4 with [(aminoethyl)aminopropyl](trimethoxy)silane. These liquid products can be used in the textile industry [45]. Poly(dimethyl-*co*-diphenyl)siloxane containing terminal aminopropyl groups was prepared through copolymerization of D_4 with $(Ph_2SiO)_4$ and $(ViMeSiO)_4$ in the presence of 1,3-bis(3-aminopropyl)tetramethyldisiloxane as a chain terminating agent. This copolymer was applied for the synthesis of a segmented poly(imide-siloxane), and further preparation of a hybrid nanocomposite reinforced with silica [46] or titania TiO_2 [47].

Methacrylic functionalized telechelic polysiloxanes (Fig. 4) were prepared in a two-step process from the telechelic glycidyl epoxy substituted polysiloxanes, that were reacted with methacrylic acid [13,48,49].

Amine terminated poly(methyl, cycloaliphatic)siloxanes: poly(dicyclopentylsiloxane-*co*-cyclopentylmethyl-siloxane) and poly(dicyclohexylsiloxane-*co*-cyclohexyl-methylsiloxane), were also prepared through a based-catalyzed ring-opening reaction of appropriate cyclosiloxanes with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (Scheme 11) or through hydrosilylation of cyclic olefins with poly(dimethylsiloxane-*co*-methylhydrosiloxane) [34,48].

Bis(aminopropyl)polysiloxanes were synthesized according to Scheme 12 as well [48,50]. For methyl, cyclopentyl, and cyclohexyl amino-functionalized siloxanes T_g was dependent on the molecular weight of the starting polysiloxanes, T_g equal to at -104, -93, and $-82\,°C$ for starting polysiloxane with $M_n = 1000$, 1200, and 1500 g/mol, respectively [50].
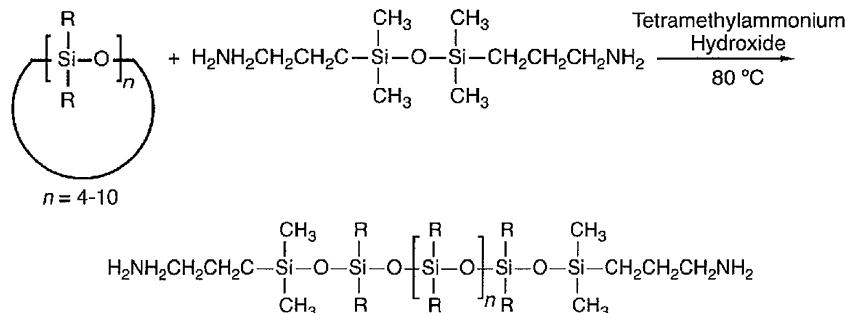
$$R = Me,\ c\text{-}C_5H_{10},\ c\text{-}C_6H_{12},\ n = 30 - 45.$$

Scheme 11. A synthetic route to amine-terminated cycloaliphatic substituted polysiloxanes. Reprinted (adapted) with permission from [34]. Copyright© 2007, Springer Science + Business Media B.V.
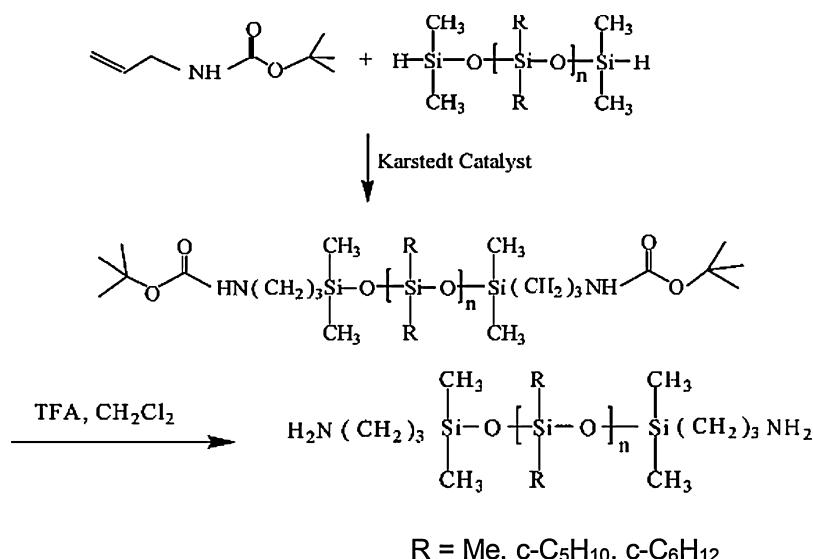
Scheme 12. The synthesis of aliphatic amine functional polysiloxanes. Reprinted (adapted) with permission from [50]. Copyright© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

CFPS containing aminoalkylfunctional side groups were also prepared by the anionic polymerization of (aminopropyl)heptamethylcyclotetrasiloxane (D_3D^{NH2}) with decamethyltetrasiloxane MD_2M ($D = Me_2SiO$, $M = Me_3SiO_{0.5}$) toward $Me_4NOSiMe_3$ (TMAS) [29,43] (Scheme 13).

The end capping reaction of α,ω-bis(hydroxy)polycaprolactone (PCL) and triblock copolymer PCL-*b*-PDMS-*b*-PCL based oligomers with 3-nitrobenzoyl chloride in a first step, followed by hydrogenation of nitro groups in the second step, was used for the preparation of the amine terminated elastomeric PCL oligomers and amine terminated PCL-*b*-PDMS-*b*-PCL copolymers (Scheme 14) [51].

Carbofunctional PDMS containing different photoactive groupings, i.e., benzoin [52], oxycyclohexene [53], glicydoxyl [54], or benzylacryl groups [55] were also prepared.

Polysiloxanes having side methacryloxy groups (MAPS) were synthesized from polymethylhydrosiloxanes (PMHS), with different contents of reactive Si—H groups through the two-step reaction (Scheme 15) [56].

Amphiphilic polysiloxane graft copolymers were successfully synthesized by the hydrosilylation reaction of poly(methylhydrosiloxane) with mono-allyl terminated poly(ethylene oxide-*co*-propylene oxide) [57]. PDMS functionalized with terminal [(trialkoxy-silane)propyl]

urethane groups were obtained in the reaction of bis (hydroxypropyl)polydimethylsiloxanes with (isocyanatopropyl)triethoxysilane [23,24].

It should be noted that this chapter is not inclusive of all examples of CFPS syntheses published in the literature.

2.3. Polyhedral functional silsesquioxanes (POSS)

Silsesquioxanes with random, ladder, cage or semi-cage structures are important hybrid materials. These polyhedral oligomeric silsesquioxanes (POSS), approximately 1–3 nm in size, are organic–inorganic molecules, described by a general formula ($RSiO_{1.5}$)$_n$ or T_n (most often: $n = 8$–12), where R is mostly an organic (preferably functional) group, that can be useful for polymerization or grafting reactions [58–63]. POSS substituted with aromatic groups exhibit a very high termal stability (>500 °C for octaphenyl-silsesquioxane).

POSS derivatives (Fig. 5) are very useful nanofillers for epoxy resins [64,65]. A variety of mono- and multiepoxy POSS monomers have been investigated, some examples of POSS structures are shown in Fig. 6. POSS can be incorporated into the epoxy network as either a junction point or a pendant group [66]. Nowadays POSS derivatives are common ingredients of engineering thermosets [64,66,67].
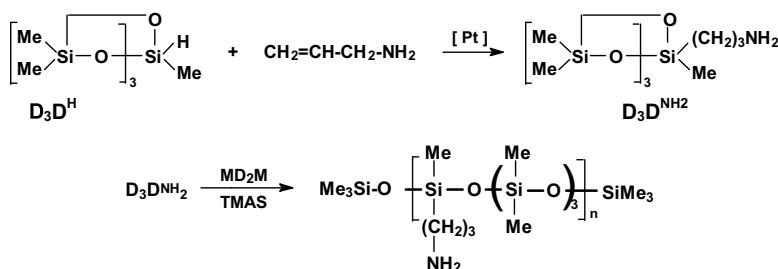
Scheme 13. The synthesis of CFPS with pendant aminopropyl functional groups [1].
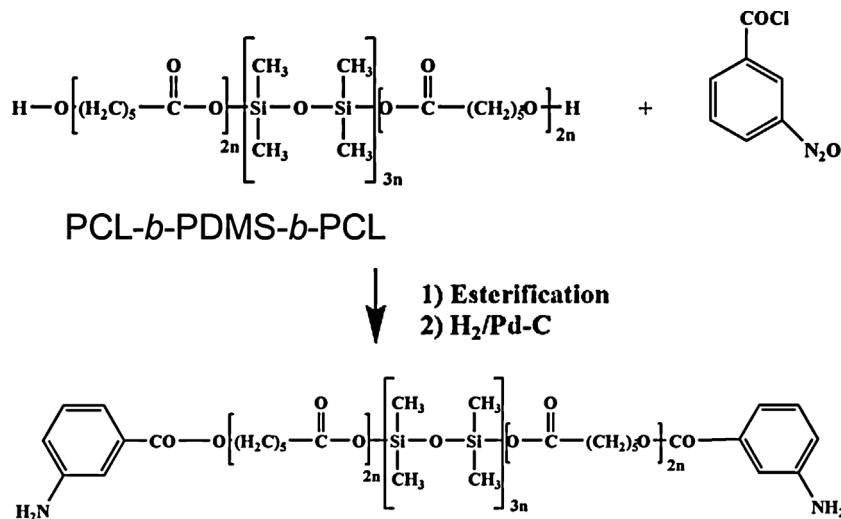
Scheme 14. The preparation of amine terminated copolymer PCL-*b*-PDMS-*b*-PCL. Reprinted (adapted) with permission from [51]. Copyright© 2009 Wiley Periodicals, Inc.

A series of novel aromatic polyhedral oligomeric silsesquioxane (POSS) dianiline molecules with different structures were synthesized from a phenyl-POSS tetrasilanol (1) and a phenyl-POSS trisilanol (2). Both of these commercially available POSS silanols react readily with appropriately substituted chlorosilanes, in the presence of triethylamine, giving the desired products in high yield. The trisilanol (2) was converted to a monosilanol (3), that was next used to prepare a POSS dianiline with an alternative

Scheme 15. The preparation of MAPS. Reprinted (adapted) with permission from [56]. Copyright© 2010, Springer Science + Business Media B.V.

architecture. A simple route to a monoaniline POSS (useful as an end-cap in polymerization) was also developed from the phenyl-POSS trisilanol [68].

Tetramethacryloxy substituted silsesquioxanes were synthesized via Pt-catalyzed hydrosilylation reaction of propargyl methacrylate with $(HSiO_{1.5})_8$ and $(HMe_2SiOSiO_{1.5})_8$. The obtained two methacrylate-functionalized cubes were viscous, clear liquids, soluble in hydrocarbons [48]. They polymerized thermally or photochemically into clear, hard hybrid polymers containing up to 65% silica [69].

Octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (OHPS) was synthesized by the direct hydrosilylation of allyl alcohol with octakis(dimethylsiloxy) octasilsesquioxane, $(HSiMe_2O)_8Si_8O_{12}$ $(Q_8M^H_8)$, toward platinum divinyltetramethyldisiloxane $[Pt_2(dvs)_3]$ as catalyst. The hydrosilylation reaction of trimethylsiloxy-2-propene with $Q_8M^H_8$, followed by desilylation reaction also gave pure OHPS. Octakis(3-methacryloxypropyldimethylsiloxy)-octasilsesquioxane (OMPS) was easily prepared directly from reaction of octakis[(3-hydroxypropyl)dimethylsiloxy)]octasilsesquioxane (OHPS) with methacryloyl chloride. Unwanted polymerization that could accompany hydrosilylation of allyl or propargyl methacrylates was first inhibited [70].

Many carbofunctional POSS derivatives are commercially available, e.g., octakis-(dimethylsiloxypropylglycidylether)silsesquioxane (OG–POSS) (Fig. 7) [71]. The latter compound was used as a reinforcing agent for polybenzoxazine nanocomposites.

A polyhedral oligomeric silsesquioxane (POSS), mercaptopropyl polyhedral oligomeric silsesquioxane (MPOSS) (Fig. 8), was synthesized through the hydrolytic condensation of (3-mercaptopropyl)triethoxysilane in an ethanol solution, catalyzed by concentrated hydrochloric acid, and was used for modification of epoxyamine networks by the cocuring reaction with DGEBA [72].

Monoaminopropyl functionalized POSS (POSS–NH_2) was prepared from reaction of POSS-triol with
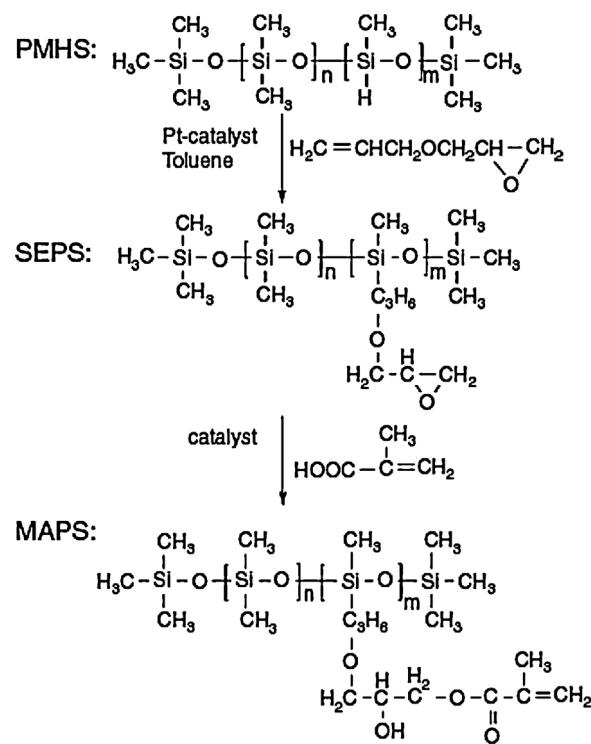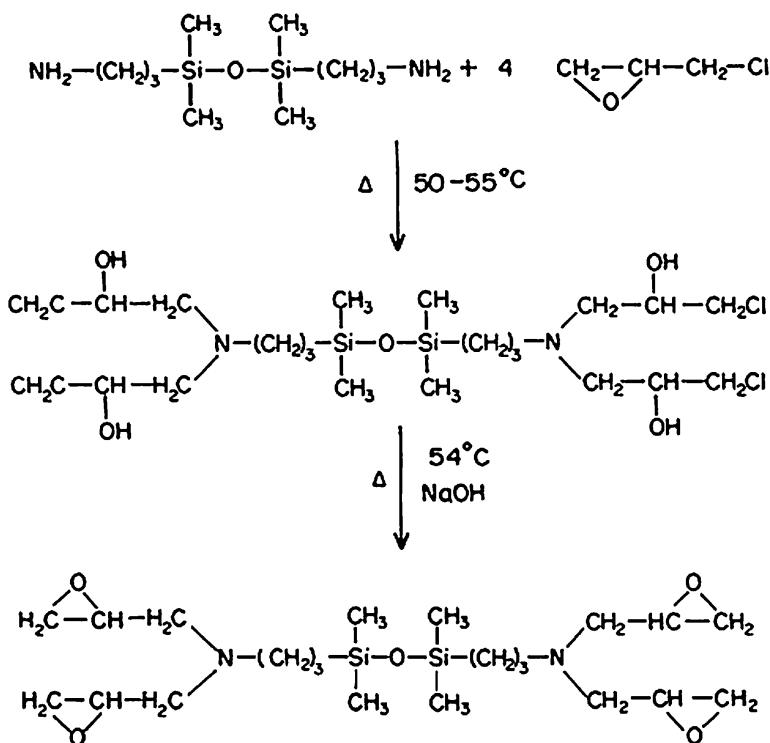
Scheme 16. The synthesis of (tetraglicidyloxy)di(aminepropyl)-1,1,3,3-tetramethyldisiloxane. Reprinted (adapted) with permission from [91]. Copyright© 2011, Springer Science + Business Media.

(aminopropyl)triethoxysilane. Polyhedral oligomeric silsesquioxane POSS–NH$_2$ served as curing and nano-reinforcement agent, providing the corrosion and fouling resistant properties in epoxy nanocoatings [73]. Multifunctional aromatic silsesquioxanes were prepared from commercially available phenyl substituted cubic Ph$_8$Si$_8$O$_{12}$. The phenyl groups on each cage were first nitrated, then reduced to produce silsesquioxanes with aniline functionality in a mixture of *ortho-*, *meta-*, and *para* locations [74,75].

Kawakami and Kakimoto reported preparation of a variety of new materials based on thermally stable phenyl groups, including dianilines (an example is shown in Fig. 9) from the octaphenyl POSS tetrasilanol Ph$_8$Si$_8$O$_{10}$(OH)$_4$ [76–78]. The patent literature also includes a complex synthesis from the tetrasilanol to dianiline derivatives [79].

The incorporation of POSS cages into polymers improved several properties of these materials such as the thermal stability, glass transition temperature, flame and heat resistance, the modulus and melt strengths. The incorporation of POSS into polymer matrices may take place during polymerization [62,80] as well as in a modification process of the final products [81]. By appropriate choice of the POSS substituents the properties of inorganic–organic hybrid polymers could be tailored according to expectations [62]. Increased oxidation resistance, surface hardening, glass transition and degradation temperatures, oxygen permeability, and reduced flammability, have been observed for linear polymers with pendant POSS molecules. Thus, increases in use temperature of this new class of nanocomposites were possible. The

POSS-hybrid materials have found many applications ranging from surface modifiers and coatings to electronic [82], optical [83], and sensor [84] applications to selectively permeability mambranes [85] and precursors for POSS nanocomposites [86].

2.4. Synthesis of epoxyfunctional silanes and siloxanes

Epoxyfunctional silanes and siloxanes (ES) are known compounds for quite a long time. Silicon compounds containing the epoxy group were prepared by: (1) epoxidation of olefinic organosilicon compounds with peracetic acid, and (2) addition of silicon hydrides across the olefinic bond of unsaturated epoxy compounds. A wide variety of epoxy groups substituted silanes or siloxanes were conveniently prepared in good yield. The epoxy and silyl functional groups of these compounds may react independently of each other [87].

Some ESs are commercially available, for example, (3-glycidoxypropyl)trimethoxysilane (GPTMS) [13,15,16,88]. Epoxy functional siloxanes offer the benefits of both silicone resins and the epoxy resins. The epoxy group can participate in curing processes of epoxies. The incorporation of siloxane into the epoxy resin results in the enhancement of physico-mechanical properties, thermal stability and anticorrosive characteristics that include good processibility, flexibility, toughness, durability, UV, chemical and weather resistance along with thermooxidative stability [89–91].

(Tetraglicidyloxy)di(aminepropyl)-1,1,3,3-tetramethyldisiloxane was prepared according to Scheme 16 [91].
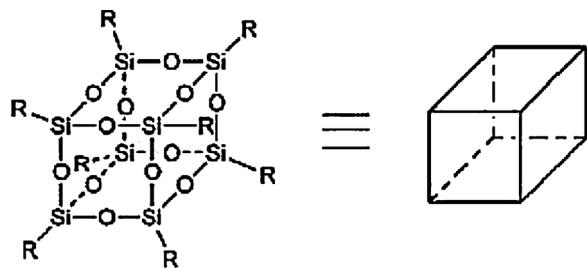
Fig. 5. The chemical structure of octasilsesquioxane T_8. Reprinted (adapted) with permission from [64]. Copyright 2011, Springer Science + Business Media B.V.

Fig. 7. The chemical structure of OG–POSS. Reprinted (adapted) with permission from [71]. Copyright 2012, Springer Science + Business Media B.V.

α,ω-Glycidyloxypropyl poly(dimethylsiloxane) (PDMS–DGE) (Fig. 10) is commercially available [92].

1,3-Bis(3-glycidyloxypropyl)-1,1,3,3-tetramethyldisiloxane (BGPTMS) (Fig. 11), 3-(3-glycidyloxypropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane, and poly(dimethyl-*co*-(glycidyloxy-propylmethyl)siloxanes were prepared via hydrosilylation reactions of allyl glycidyl ether with appropriate hydrosiloxanes and PDMS-*co*-PMHS, catalyzed by rhodium complex [{Rh(OSiMe₃)cod}₂]

[93–95]. BGPTMS was used in epoxy resin compositions [95].

Poly[(glycidyloxypropyl, methyl)-*co*-dimethyl]siloxane was synthesized from appropriate PMHS and allyl glycidyl ether and was applied as an ingredient of epoxy composites [95]. A series of bis(glycidyloxypropyl)polysiloxanes bearing methyl, cyclopentenyl and cyclohexenyl substituents at silicon (Fig. 12) were prepared by the hydrosilylation reaction of hydride-terminated polysiloxanes with allyl glycidyl ether in the presence of Karstedt catalyst [48].

The functionalization of hydride terminated poly (dicyclopentylsiloxane-*co*-cyclopentyl-hydrosiloxane) and poly
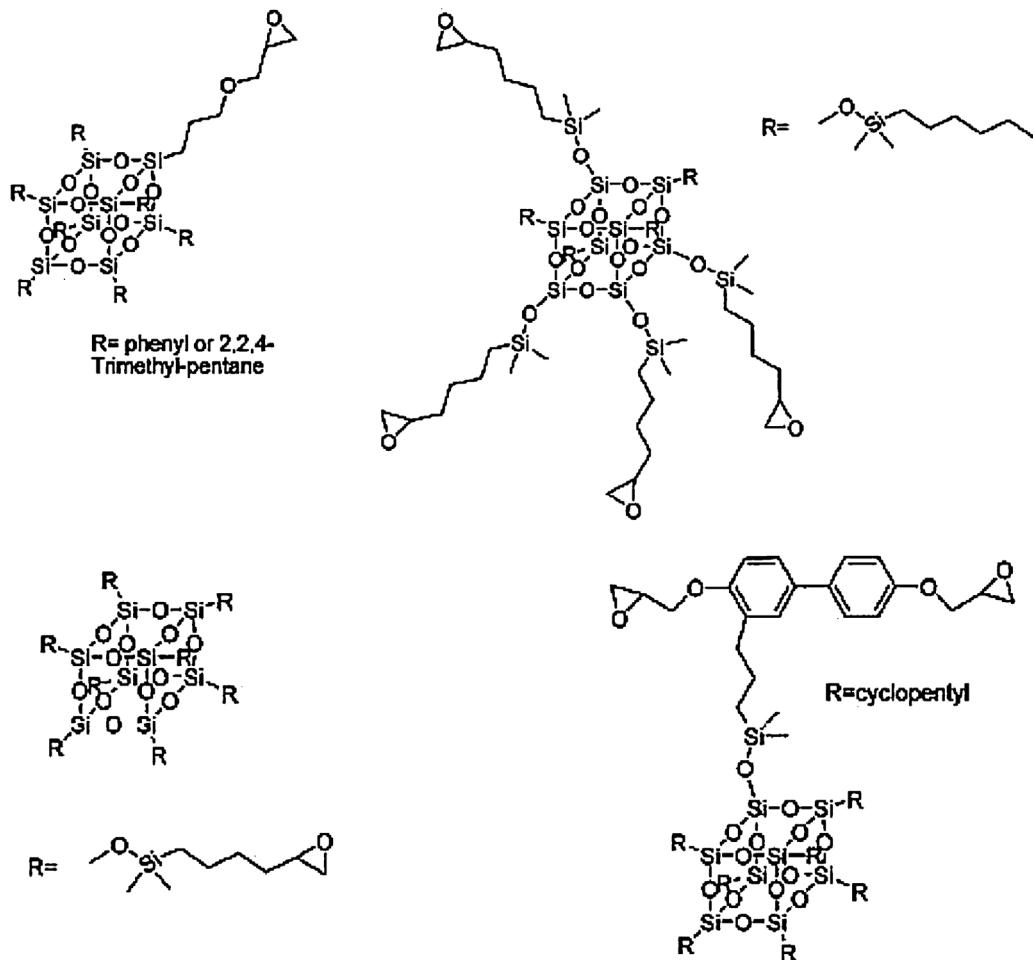
Fig. 6. Examples of mono- and multi-functional epoxy–POSS monomers. Reprinted (adapted) with permissions from [64,66]. Copyrights: 2004, American Chemical Society, and 2011, Springer Science + Business Media B.V.
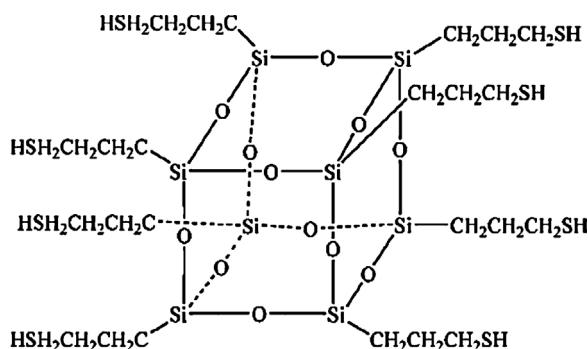
Fig. 8. The chemical structure of MPOSS. Reprinted (adapted) with permission from [72]. Copyright 2008 Wiley Periodicals, Inc.
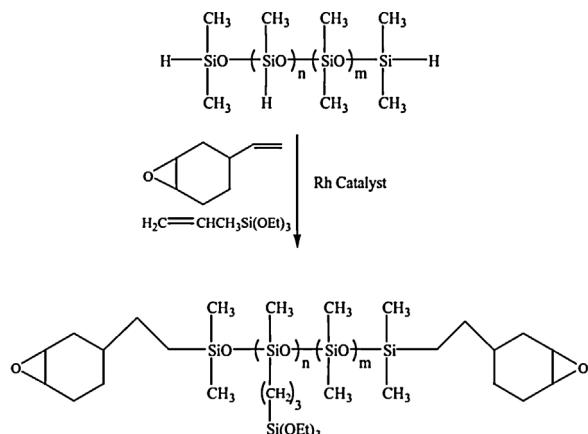
Scheme 17. The synthesis of telechelic cycloaliphatic epoxy and (alkoxy)silane functionalized polysiloxanes. Reprinted (adapted) with permissions from [96,97]. Copyrights: 2003, Elsevier, and (2004), American Chemical Society.

(dicyclohexylsiloxane-*co*-cyclohexylhydrosiloxane) with epoxy and alkoxy functional groups has also been described (Scheme 17) [34,48,96,97].

The pendant alkoxysilane enabled miscibility during formulation, moisture-curing and provided a site for interaction with the metal/silicon-oxo-cluster, while the
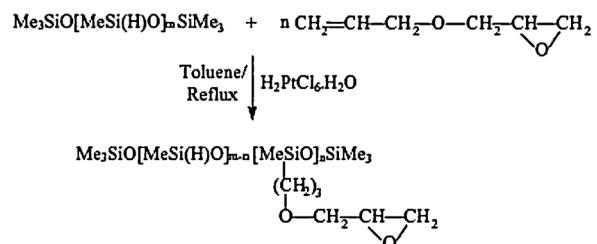
Scheme 18. The preparation of epoxy functionalized polysiloxanes. Reprinted (adapted) with permission from [98]. Copyright© 2004, Elsevier.
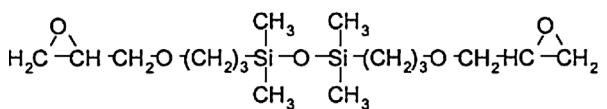
Fig. 11. The structure of 1,3-bis(glycidyloxypropyl)-1,1,3,3-tetramethyldisiloxane (BGPTMS). Reprinted (adapted) with permission from [95]. Copyright 2012, Elsevier.

$R = Me, c-C_5H_{10}, c-C_6H_{12}$
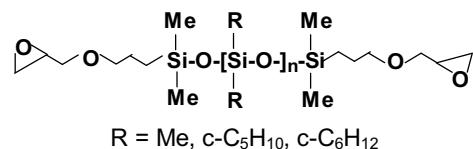
Fig. 12. The chemical structure of epoxy functionalized polysiloxane. Reprinted (adapted) with permission from [50]. Copyright 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

cycloaliphatic epoxide provided a crosslinking site for cationic UV-induced cure. The cycloaliphatic silicones were UV-cured with mixed sol–gel precursors for usage as aerospace coatings and were ambient temperature-cured, and can be applied as antifouling coatings. The cycloaliphatic silicones were low surface energy and good surface tension additives.

The epoxy functionalized polymethylsiloxane (Scheme 18) was prepared by reaction of poly(methylhydrosiloxane) (PMHS) with allyl-2,3-epoxypropylether in the presence of a platinum catalyst [98].
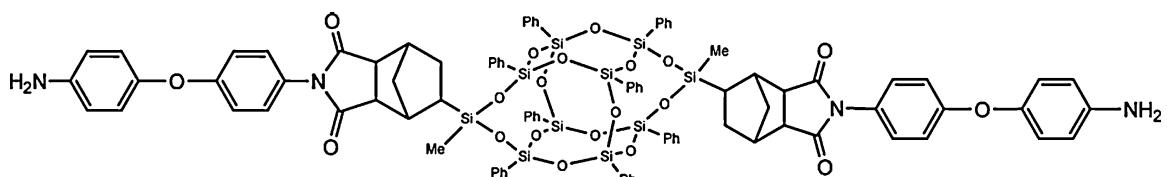
Fig. 9. The structure of POSS–dianiline derivative. Reprinted (adapted) with permission from [77]. Copyright (2007) American Chemical Society.
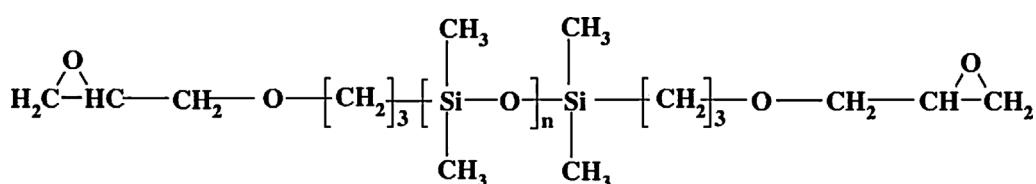
Fig. 10. The chemical structure of PDMS–DGE. Reprinted (adapted) with permission from [92]. Copyright 2007, Elsevier.
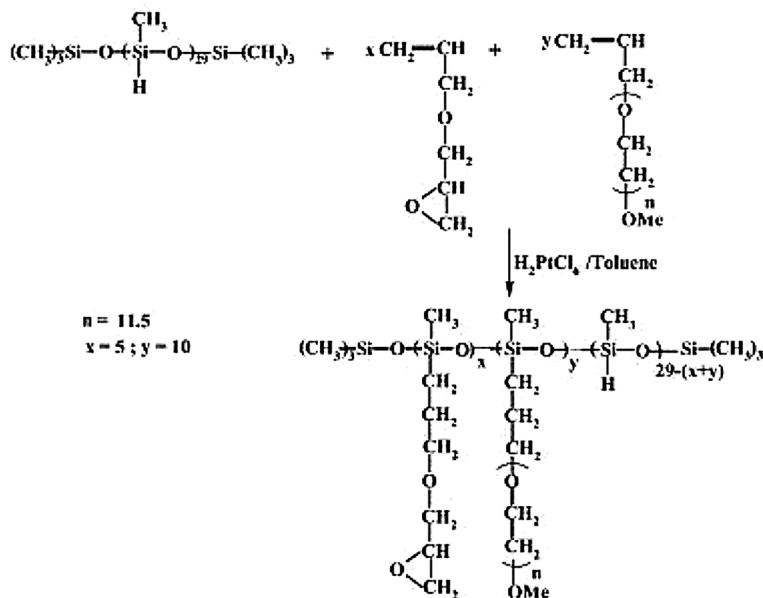
Scheme 19. The preparation of epoxy-functionalized amphiphilic PEG-siloxanes. Reprinted (adapted) with permission from [100]. Copyright© 2007 Wiley Periodicals, Inc.

A series of 3′,3′,3′-trifluoropropyl substituted 1,9-bis [glycidyloxypropyl]pentasiloxanes and 1′H,1′H,2′H,2′H-perfluorooctyl groups were prepared by the platinum (Karstedt) catalyzed hydrosilylation reaction of 1,9-dihydrido-decamethylpentasiloxane, 1,9-dihydrido-3,5,7-tris-(3′,3′,3′-trifluoropropyl)-heptamethylpentasiloxane, and 1,9-dihydrido-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane with allyl glycidyl ether [99].

Epoxy-functionalized amphiphilic PEG-siloxanes were synthesized by hydrosilylation of allyl 2,3-epoxy propyl ether (AEPE) and allyl monomethoxy poly(ethylene glycol) (AMPEG) with appropriate PMHS (Scheme 19), in the presence of the Speier's catalyst, at 100 °C for 72 h [100].

The thermal stability of the epoxy-functionalized siloxane and epoxy-functionalized poly(ethylene glycol) (PEG), containing 20 mol.% PEG, was studied by the thermogravimetric analysis. The epoxy-functionalized PDMS showed an initial degradation at 250 °C, whereas for PEG-incorporated PDMS the degradation began at 237 °C.

A reactive hyperbranched polysiloxane terminated by epoxy groups (with molecular weight 9320 g/mol and viscosity of 295 mPa s) was synthesized through the hydrolysis of (3-glycidoxypropyl)(trimethoxy)silane [101].

POSS epoxy hybrid composites have attracted much research interest because of their unique structure, versatile synthetic routes, and changeable properties. The unique thermal and mechanical properties of POSS composites make them potential candidates for applications in high temperature and temperature variable environments [102]. Octa(propyl-glycidyl ether) polyhedral oligomeric silsesquioxane (OE-POSS) was prepared as a viscous liquid by Zheng and Liu via hydrosilylation of $H_8Si_8O_{12}$ with allyl glycidyl ether in the presence of Karstedt's catalyst (Scheme 20) with a high yield: 94% [103]. ^{29}Si NMR data showed that OE-POSS was formed, mainly as a β-addition isomer.

Other epoxide silsesquioxanes were obtained by the Pt-catalyzed hydrosilylation of allyl glycidyl ether (AGE) with $(HMe_2SiOSiO_{1.5})_8$ $(Q_8M^H_8)$ and $(HSiO_{1.5})_8$ (T^H_8). The yields of reactions were high (>90%) and relatively pure products were formed as determined by ^{1}H-, ^{13}C-, and ^{29}Si NMR, TGA, FTIR, and SEC. $Q_8M^H_8$ and T^H_8 were reacted with 4 or 8 equivalents of AGE using Karstedt's catalyst [Pt(dvs)]. Four sets of products, $Q_8M^H_4M^E_4$, $Q_8M^E_8$, $T^H_4T^E_4$, and $T^H_1T^E_7$, were isolated. Products with an average four substitutions per cube: $T^H_4T^E_4$ and $Q_8M^H_4M^E_4$ consisted of a series of
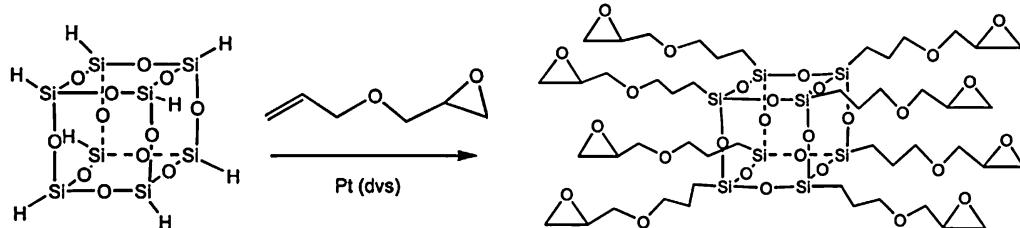
Scheme 20. The synthesis of $H_8Si_8O_{12}$ and OE-POSS. Reprinted (adapted) with permission from [103]. Copyright© 2005 Wiley Periodicals, Inc.
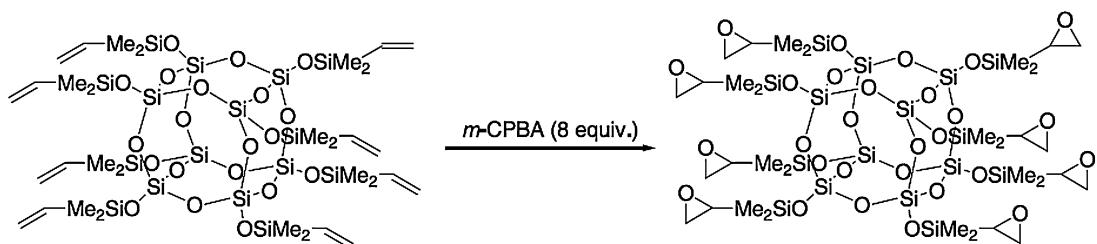
Scheme 21. The synthesis of the epoxy group containing POSS by epoxidation of the vinyl groups. Reprinted (adapted) with permission from [106]. Copyright© 1996, Elsevier.

oligomers (from mono to septa substituted) comprising that average. Efforts to fully substitute T^H_8 gave only $T^H_1T^E_7$ based on NMR, TGA, and FTIR analyses [104]. Octaglycidyl-silsesquioxane ($Q_8M^E_8$) was a liquid with a viscosity of ~300 cps [105].

Zhang and Laine epoxidized quantitatively octavinyloc-tasilsesquioxane (vinylSiO$_{1.5}$)$_8$ and [(vinylMe$_2$SiO)SiO$_{1.5}$]$_8$ with a large exsess of m-chloroperoxybenzoic acid (m-CPBA) per cube (Scheme 21). The [(vinylMe$_2$SiO)SiO$_{1.5}$]$_8$ compound converted quantitatively to the octaepoxide, [(epoxyMe$_2$SiO)SiO$_{1.5}$]$_8$.

Partial epoxidation was achieved with only three equivalents of m-CPBA. The partially epoxidized compound had an average of two epoxy groups per cube. Both polyepox-ides easily polymerized in the presence of amines or Lewis acid catalysts. Thus, they could be used as potential coupling agents in the synthesis of novel inorganic–organic hybrids [106].

(Octaglycidylether)propyl and hepta(3,3,3-trifluoro-propyl)glycidyletherpropyl polyhedral oligomeric silsesquioxanes (Schemes 22 and 23) were synthesized via the hydrosilylation reactions of allyl glycidyl ether with octahydrosilsesquioxane (HSiO$_{1.5}$)$_8$ (T^H_8) or hepta(3,3,3-trifluoropropyl)hydrosilsesquioxane [102].

The ladderlike poly(epoxysiloxanes) with different side groups grafted on the ladderlike backbones were also synthesized. However, the synthetic procedure was not described. Unlike common silicone polymers and epoxies, these polymers have ladderlike chains and

combine both silicone and epoxy properties [108,109]. Another example is the preparation of poly(methyl-co-glycidoxy)silsesquioxane by grafting allyl glycidyl ether to a ladder-like polysilsesquioxane via the hydrosilyla-tion reaction, catalyzed by [Cp$_2$PtCl$_2$] [110], according to Scheme 24:

Hybrid organic–inorganic materials containing ladder silsesquioxane segments were obtained by cohydroly-sis of (3-glycidoxypropyl)trimethoxysilane (GPTMS) and tetraethyl orthosilicate (TEOS) in an acidic medium (Scheme 25) [111]. The addition of BF$_3$·OEt$_2$ catalyzed the epoxide rings opening polymerization and the formation of a poly(ethylene oxide) network at room temperature, without formation of diol units or boric acid precipitation in the final product. BF$_3$·OEt$_2$ also had a catalytic effect on the formation of the inorganic oxide network and caused increasing the cross-linking density. The prereaction time of GPTMS with TEOS was found to be an important parameter [111].

The product obtained was applied in the modification of a cyanate ester resin (CE). The CE-polysiloxane resin (CE/E-Si) showed significantly different curing behavior, thermal, mechanical, and water-absorbing properties due to the change of the network structure. The CE/E-Si resins exhibited better processing property, such as a much lower curing temperature than neat CE and CE/EP systems, drastically improved toughness and water resistance. Moreover, T_g and the initial degradation temperature of CE/E-Si resins were lower than those of original CEs [43].
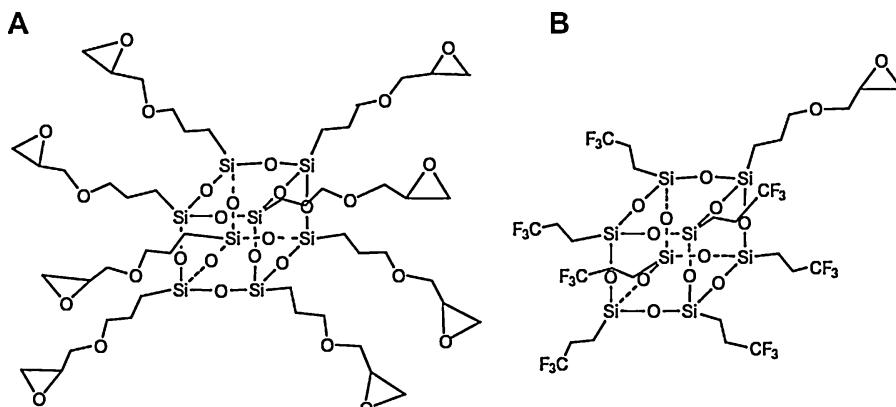
Scheme 22. The chemical structures of the POSS macromers: (A) octaglycidylether POSS, (B) hepta(3,3,3-trifluoropropyl) glycidyletherpropyl POSS. Reprinted (adapted) with permission from [102]. Copyright© 2006, Elsevier.
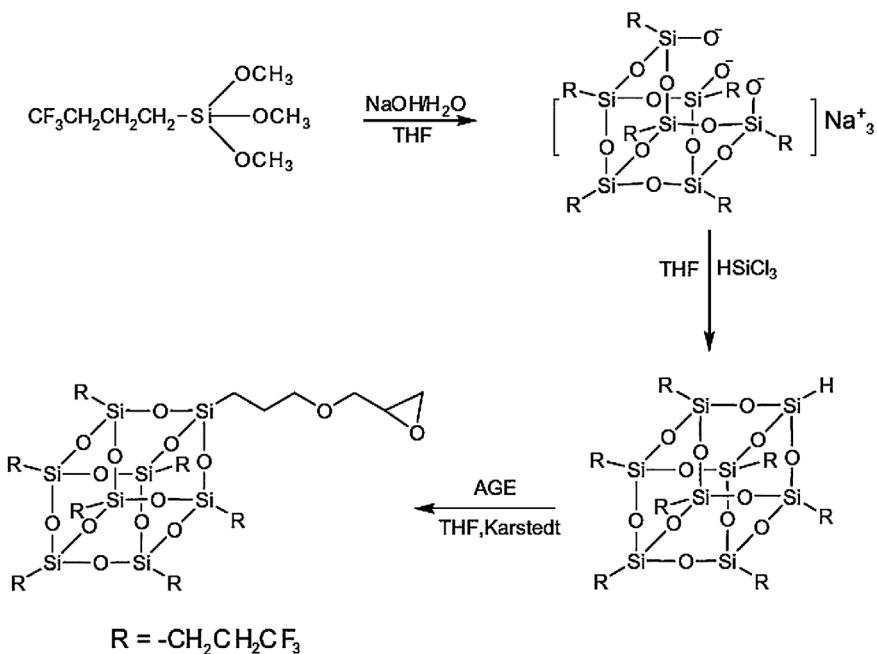
Scheme 23. The synthesis of hepta(3,3,3-trifluropropyl) glycidyletherpropyl POSS [102]. Reprinted (adapted) with permission from [102]. Copyright© 2006, Elsevier.
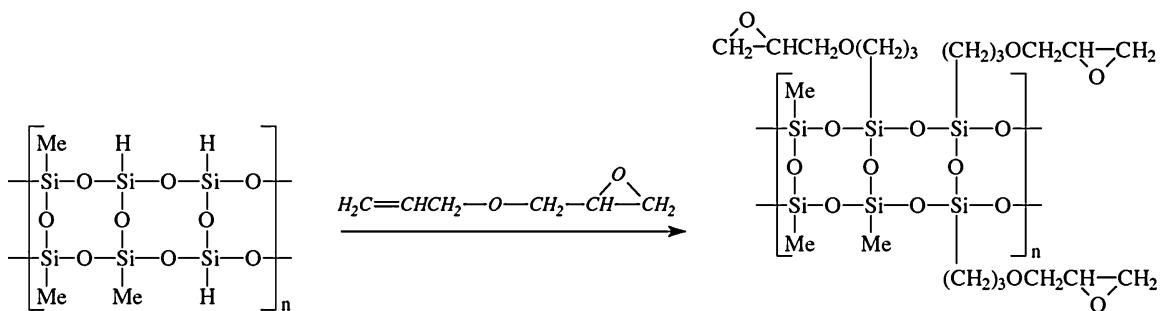
Scheme 24. The preparation of poly(dimethyl-co-glycidoxy)silsesquioxane. Reprinted (adapted) with permission from [110]. Copyright© 2000, Elsevier.

Aminopropyl-substituted polymethylsiloxane was synthesized by the equilibration (at 125 °C) of siloxane monomers: (3-aminopropyl)(diethoxy)methylsilane H_2N $(CH_2)_3MeSi(OEt)_2$ (AMDES) with Me_2SiO_4 (D_4) and $Me_3SiOSiMe_3$ (MM) [43]. In the next step multifunctional epoxidized polysiloxane (E-Si) was prepared via the reaction between (aminopropyl)-polymethylsiloxane and

the epoxy resin at the reflux temperature of 2-butanone (Scheme 26).

1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido) propyl]tetramethyldisiloxane (BISE), bearing a cycloaliphatic imide ring, was prepared from 1,3-bis(3-aminopropyl)-tetramethyldisiloxane and tetrahydrophthalic anhydride by a two-step method (Scheme 27) [47].
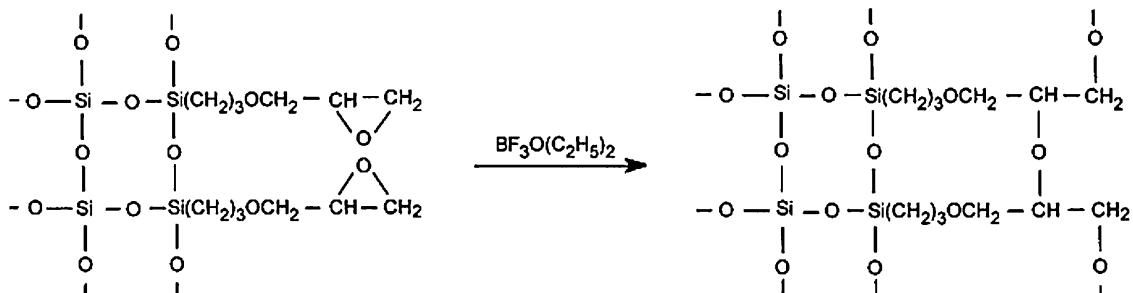
Scheme 25. The formation of a cross-linked hybrid organic–inorganic network. Reprinted (adapted) with permission from [111]. Copyright (1999) American Chemical Society.
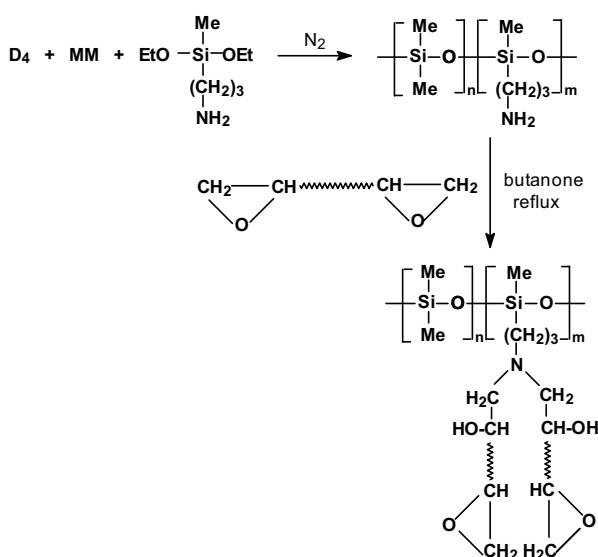
Scheme 26. The synthesis of E-Si resin.

Scheme 28. The synthesis of 1,4-bis-silyloxybenzene oligomers with terminal silanol, hydride and methoxy functional groups. Reprinted (adapted) with permission from [112]. Copyright© 2007, Rights Managed by Nature Publishing Group.

1,4-Bis[(glycidyl- or cyclohexene oxide-functionalized alkyl)methylhydrosilyl]benzene and methyldimethoxysilanes with epoxy groups were synthesized by hydrosilylation of 1,4-bis(methyldihydrosilyl)benzene and methyldimethoxysilane with olefin-functionalized alkyl epoxy derivatives in the presence of a platinum catalyst [112]. 1,4-Bis-silyloxybenzene oligomers with terminal silanol, hydride and methoxy functional groups were obtained by subsequent hydrolysis and methanolysis of the hydrosilyl derivatives (Scheme 28).

Poly(silphenylenesiloxane)s with epoxy side groups were synthesized by heteropolycondensation of the hydrosilane, silanol and methoxysilane functional groups in the prepolymer and 1,4-bis[(epoxy-functionalized alkyl)methylsilyl]benzene, or 1,1-dimethoxy(epoxy-functionalized alkyl)methylsilane (Schemes 29 and 30), in the

Scheme 27. The synthesis of BISE. Reprinted (adapted) with permission from [47]. Copyright© 2007, Elsevier.

presence of tris-(pentafluorophenyl)borane as the catalyst [112].

A silsesquioxane functionalized with carboxyl ester groups (Fig. 13) was synthesized by reacting the silsesquioxane, functionalized with secondary hydroxyl groups, with a stoichiometric amount of an acid anhydride.

The carboxyl-functionalized silsesquioxanes contained of 8–11 silicon atoms and two carboxyl ester groups per organic branch (from 16 to 22 carboxyl groups per molecule). It was a stable glassy product at room temperature, showing good solubility in a variety of organic solvents. It was used as a modifier of epoxy networks based on DGEBA cured with 4-(dimethylamino)pyridine (DMAP) [113].

The diepoxide-functionalized POSS macromer, diglycidyloxypropyl double-decker silsesquioxane (DDSQ) was prepared by a three-step method (Scheme 31) [114]. Octaphenyldicyclooctasiloxane tetrasodium silanolate $Na_4O_{14}Si_8(C_6H_5)_8$ was synthesized by the method described by Kakimoto and coworkers [115].

The coupling reaction between $Na_4O_{14}Si_8(C_6H_5)_8$ and methyldichlorosilane ($HSiCH_3Cl_2$) afforded 3,13-dihydrooctaphenyl DDSQ (dihydro DDSQ). In the next step, the hydrosilylation reaction between dihydrosilyl DDSQ and allyl glycidyl ether (AGE) was carried out, providing (3,13-diglycidyloxypropyl)octaphenyl double-decker silsesquioxane (diglycidyloxypropyl DDSQ) [114].

3. Properties and applications of epoxy resins

Epoxy resin, based on bisphenol A diglicydyl ether (DGEBA) (Fig. 14), is one of the most widely used thermosetting resins. It has several useful properties such as high tensile strength and modulus, low shrinkage, good adhesion and insulation property, and excellent chemical corrosion resistance.

Epoxy resins are important engineering polymeric materials. They have especially relatively good thermal stability, combined with high stiffness and strength at
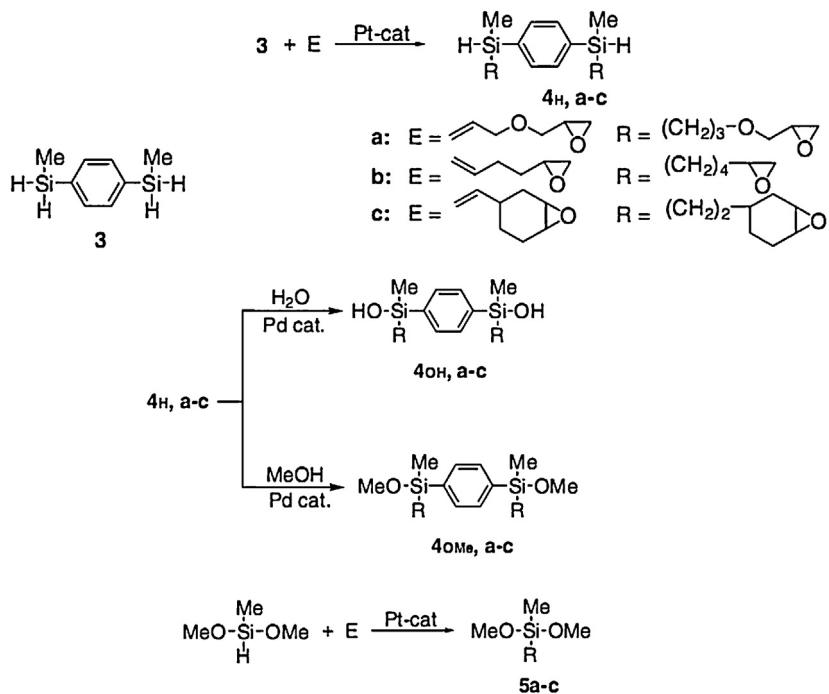
Scheme 29. The synthesis of 1,4-bis-(glycidyloxy)silyloxybenzene and 1,4-bis-(cyclohexene oxide)silyloxybenzene oligomers. Reprinted (adapted) with permission from [112]. Copyright© 2007, Rights Managed by Nature Publishing Group.

low creep. Among the various polymer matrices available, epoxy resins remain dominant in the development of high performance materials due to their thermal stability, mechanical properties, and processability. They are frequently used in applications where tough, durable coatings or adhesives are needed, as the chemical structure of the epoxy resins impart a high chemical resistance against a wide range of severe corrosive conditions. The cured epoxy resins have highly crosslinked networks that show high modulus and fracture strength, low creep, and good performance at elevated temperatures. Thus, they are useful in various fields of engineering, such as in the electrical

industry, for structural applications in both the commercial and military aircraft industries. Cross-linking increases the rigidity the molecular network of the epoxy resins, decreases their deformability, and increases the process-induced shrinkage [116–118].

Epoxy resins have been commercially available for about 50 years and are widely used in modern industries. Epoxy resins have satisfactory mechanical properties, good chemical, thermal, and weather resistance, so they find many practical applications: as adhesives, surface, coating and painting materials, composites, molding compounds, microelectronic materials, printed circuit boards, and matrices for advanced fiber-reinforced composites [116–118]. Transparent epoxy resins, based on **DGEBA**, cured by anhydride acids, are commonly used in the light emitting diodes (LED) encapsulation [119,120].

The outdoor applications of aromatic epoxides, bearing strong UV chromophore groups, are limited. Moreover, they always contain chloride atoms because they are synthesized in the polycondensation reaction of epichlorohydrin with phenols, while the aliphatic and cycloaliphatic epoxy resins (CER) are usually synthesized by peracid oxidation of olefins. Consequently, because they do not contain strong UV chromophore groups in their structure, they are highly resistant to ultraviolet light. CER can be applied in the microelectronic packaging without the risk of microcircuit corrosion. They have found different applications: as reactive diluents, paints, inks, vacuum-pressure impregnation of coils, and printed circuit-board coatings, because of their good chemical and heat resistance, good dielectric and mechanical properties, as well as excellent processability. However, some features of cycloaliphatic
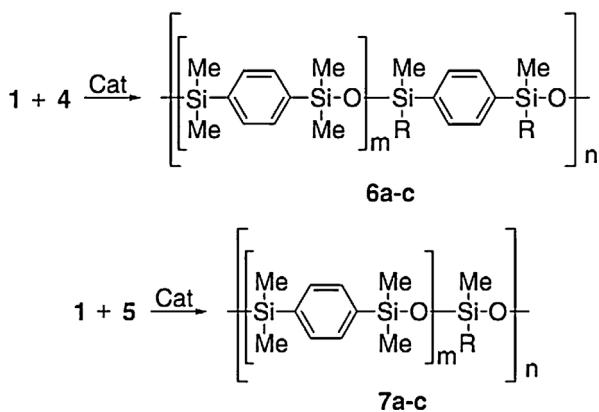
Scheme 30. The synthesis of poly(silphenylenesiloxane)s with epoxy side groups. Reprinted (adapted) with permission from [112]. Copyright© 2007, Rights Managed by Nature Publishing Group.
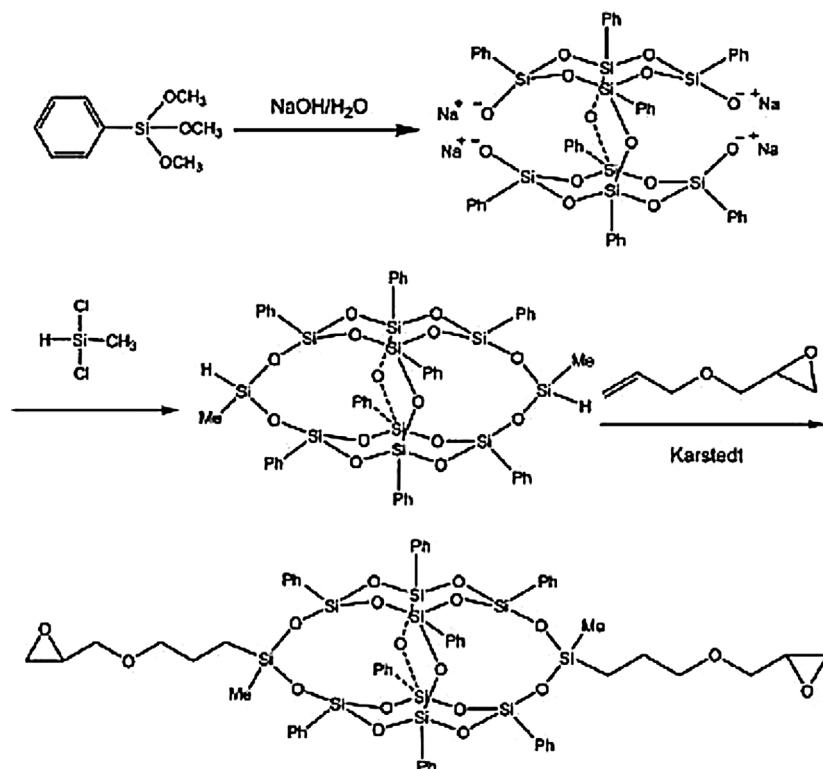
Scheme 31. The synthesis of 3,13-diglycidyloxypropyloctaphenyl DDSQ. Reprinted (adapted) with permission from [114]. Copyright© 2011, Royal Chemical Society.
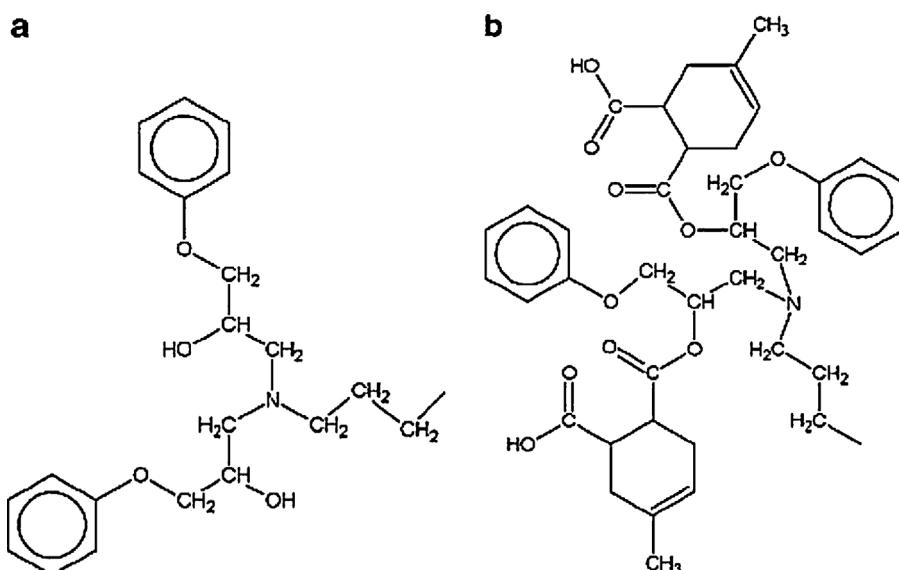
Fig. 13. The chemical structures of the organic branched groups of silsesquioxanes functionalized with: (a) secondary OH groups and (b) carboxyl ester groups. Reprinted (adapted) with permission from [113]. Copyright 2000, Elsevier.
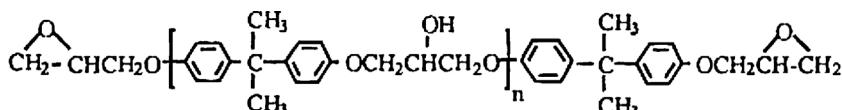
Fig. 14. The molecular structure of DGEBA.

epoxy resins, e.g., electrical insulating properties and resistance against moisture require improvement before their application in advanced electronics [47].

Nevertheless, epoxy resins also have some disadvantages that limit their high-performance applications. Recent developments in electronic packaging industries require some superior properties for epoxy-based materials, such as strong thermal stability, low shrinking stress, low dielectric constant, and low thermal expansion coefficients. The applications of epoxy resins as electronic materials and in the aerospace industry, require an improvement of their thermal and flame resistance [72,107,121–124].

Highly cross-linked polymer systems are usually brittle and have limited utility in applications requiring high impact and fracture strength. Therefore enhancing the fracture toughness of epoxy resins is an important objective [65,125]. The cross-linked epoxy resins are combustible and their combustion is self-supporting. The fire risk is a major drawback of epoxy resins and recently the research efforts have focused on improving their thermal stability, increasing glass transition temperatures and enhancing flame retardancy [126–128]. Currently, research on epoxy resins have focused on improving their mechanical properties, thermal stability and flame resistance, raising glass transition temperatures (T_g), lowering their dielectric constant and a coefficient of thermal expansion (CTE).

Strzelec et al. [129] showed that the application of new mercaptan-terminated polythiourethane hardeners improved the flexibility of epoxy resins along with increased tensile strength and impact toughness. The polythiourethane hardeners gave a homogeneous system with epoxy resins and had good storage stability with other coreactants, such as diamines. The incorporation of polythiourethanes into the epoxy resins enhanced the values of the impact resistance and tensile strength. Flexibility was imparted by the presence of the aliphatic polyether chains that separated the rigid aromatic rings of the epoxy molecules and provided greater degrees of freedom for the chains. The presence of flexible and free rotation of such linkages decreased the T_g values of the mercaptan modified resins. When higher percentages of polythiourethanes were used, extremely flexible rubber-like compounds were obtained. With ratios lower than 50 phr of polythiourethane, resilent impact resistant epoxy materials were prepared [129].

4. Epoxy resins modified with reactive silanes and siloxanes

Carbofunctional silanes, siloxanes and polysiloxanes are useful in the modification of the properties of epoxy resins [1]. An application of the functional silanes and siloxanes and silane modified fillers significantly and positively affects properties of the cross-linked epoxides and their numerous composites and nanocomposites. For instance, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (DS) was used as a liquid epoxy curing agent of epoxy molding compounds (EMCs) for high-reliability semiconductor devices. Experimental results indicated that DS could be effectively used as the

epoxy curing agent and greatly decrease the viscosity of epoxy system. This way, the coefficient of thermal expansion (CTE) of EMCs was lowered effectively by increasing the filler loading. The concentration of DS strongly affected the mechanical properties of the thermally cured epoxy composites. As expected, the flexural modulus decreased and the toughness of epoxy composite was improved [130].

Introducing polyether side chains into the polysiloxane improved the miscibility between a polysiloxane and epoxy matrix. The graft copolymer exhibited increased epoxy-miscible with increased poyether content. Compared with the neat epoxy network, the T_gs of the polysiloxane modified epoxies decreased and with the increase in polyether content, the decreasing trend of T_g became smaller. The amphiphilic graft copolymer can form microspheres in the epoxy resin, mainly dependent on the polyether content in the graft copolymer and the graft copolymer content in the epoxy resin. The microphase separation follows self-assembly and reaction induced mechanisms and it is strongly dependent on the miscibility of graft copolymer with the epoxy matrix. Moreover, the tensile and impact strength of epoxy resins can be greatly improved by introducing a low amount of graft copolymer with proper polyether content [29].

The epoxy resin and different amounts of elastomeric polycaprolactone (PCL), and amine terminated PCL-*b*-PDMS-*b*-PCL copolymer, were mixed with diaminodiphenyl sulfone (DDS) and cured [50]. Effects of molecular structure and concentrations of reactive ingredients on the mechanical and thermal properties of cured epoxy networks were observed. The mechanical properties (impact, tensile, and flexural strength) and thermal properties (glass transition temperatures and thermal stability) of the epoxy resin-toughener systems were dependent on the concentrations and the structure of reactive PCL oligomers and PCL-*b*-PDMS-*b*-PCL copolymers. This modification of epoxy resins led increased impact strength and showed no adverse effect on the mechanical and thermal properties of the cured epoxy resins. The optimal composition for improvement of the impact strength of the epoxy matrix was achieved at 10 wt.% PCL and 3 wt.% PCL-*b*-PDMS-*b*-PCL.

The thermooxidative decomposition temperatures of resins toughened by PCL and PCL-*b*-PDMS-*b*-PCL were only slightly higher that of a neat epoxy network. The amounts of % residue after thermal decomposition were relatively higher because of polymeric moiety in reactive oligomers. As expected, the T_g values of toughened resins slightly decreased with the increasing content of reactive oligomers. The heterogenity of the cured epoxy resins was observed, but a presence of two-phase morphology in the toughened systems was not observed, that suggested that the oligomers were chemically bound to the epoxy resin [50].

The powder molding compositions with a low stress without significantly sacrificing T_g were made from the epoxy resin, curing agent, a polylactone-polysiloxane block copolymer and a filler. These materials may be used as coatings in which low stress properties are desired [131].

Cabanelas et al. [132] cured bisphenol-A diglycidyl ether (DGEBA) with aminopropyl grafted polymethylsiloxane (PAMS) containing 15 wt.% of cyclics fraction. The water

absorption properties of a new epoxy formulation were studied. It was shown that equilibrium properties of epoxy resins cured with PAMS at different temperatures were greatly enhanced. Due to the special characteristics and morphology of this epoxy system [39], a different behavior against postcuring temperature was found. Samples were cured at 120 °C for 1 h and postcured 1 h at 130 and 150 °C. A second set of samples were cured 2 h at 60 °C and postcured 1 h at 80, 100 and 120 °C. Samples postcured at 60 and 80 °C showed the highest increase in conversion, due to different reasons:

(a) water acted as a plasticizing agent; as a consequence T_g decreased and reaction became possible,
(b) a temperature effect was observed (the bath of water was thermostated at 50 °C), relatively near the T_g of the samples less cured, and reaction continued at very long times.

Cross-linking of a solution cast film of poly(silphenylenesiloxane)s having epoxy side groups with 1,4-diaminobenzene gave stretchable film with higher thermal stability than that of the starting epoxy resin [112].

4.1. Modification of epoxy resins with epoxyfunctional silanes and siloxanes

Epoxy resins have been successfully crosslinked by copolymerization with epoxy-functional silanes and siloxanes. New hybrid materials were obtained by a photocrosslinking process of epoxy functional trialkoxysilanes, followed by hydrolysis and sol–gel polycondensation [96,133].

The monomer 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)propyl]tetramethyldisiloxane (BISE) containing imide ring and siloxane moiety was prepared by Tao et al. [47] in order to improve the properties of aliphatic epoxides. The hydrophobic siloxane segment was introduced to improve the dielectric properties and the resistance against moisture, while the rigid imide ring could improve the thermal stability. The epoxy resins and BISE were thermally cured with alicyclic anhydrides: hexahydro-4-methyl-phthalic anhydride and hexahydrophthalic anhydride. The cured resins showed relatively low T_g, that was affected by the flexible propyl and siloxane segments in BISE molecule. Good thermal stability was confirmed by the decomposition temperature ∼350 °C at 5% weight loss in nitrogen atmosphere. The modification of epoxy resin with BISE gave materials with good mechanical and dielectric properties as well as low water absorption in comparison with the cured commercial cycloaliphatic epoxy resins. The flexural strengths of crosslinked resins reached 63–82 MPa and the tensile strengths: 31–33 MPa [47].

Preliminary UV curing tests of the (α,ω-glycidoxypropyl)polydimethylsiloxane (PDMS–DGE) phase in the presence of a cationic photoinitiator showed that PVAc/PDMS two-phase coatings can be obtained, without any solvent emission [92]. The coatings obtained increased the density of the native aerogels by a factor of 2–3, but the strength of the resulting materials may increase by more than 2 orders of magnitude. Processing variables such as the amount of APTES used to make the gels, the epoxy type and concentration used for crosslinking, the cross-linking temperature, and time were varied according to a multivariable design-of-experiments (DOE) model.

Coating materials, having improved resistance to degradation of electric properties by boiling water and moisture, were prepared from the epoxy resin (DGEBA), modified with hydroxyl-functionalized polymethylphenylsiloxane resin, alkoxy functional polymethylsiloxane, silane coupling agents bearing amino and epoxy groups, and carboxylic acid anhydride as the curing agent [134].

A reactive hyperbranched polysiloxane (HPSiE) terminated by epoxy groups [101] was used to develop a novel high performance modified bismaleide-triazine resin (BT), that was expected to have the combined advantages of both hyperbranched polymers and BT resins, and thus the resultant new resin system showed excellent dielectric properties, good toughness, high temperature resistance, and low water absorption [135]. Organic–inorganic composites showing improved properties at elevated temperatures were obtained from epoxy resin (DGEBA), APTES, IPTES and TEOS as the silicone dioxide precursor [136].

Organic–inorganic hybrids were prepared with a DGEBA type epoxy and silane-modified isocyanuric acid triglycidyl ester via a sol–gel process. The epoxy resin was modified by (3-isocyanatopropyl)triethoxysilane (IPTES), that improved the compatibility of the organic and inorganic phases (Schemes 32–34) [137]. The thermal stability of the hybrids increased with the contents of the inorganic components and incorporation of silicon and nitrogen into the network of hybrids.

A novel methodology was elaborated for the preparation of interpenetrating polymer networks (IPNs) of an epoxy resin (DGEBA) and polydimethylsiloxane (PDMS) [138].

The vinyl-terminated PDMS (vinyl-PDMS) was partially cross-linked with PDMS containing hydrosiloxane units (H-PDMS) (Fig. 15) and further reacted with DGEBA, modified silica (m-silica) (Scheme 35), and methyl tetrahydrophtalic anhydride (MTHPA) as the curing agent. Subsequently, the curing reactions of the DGEBA/m-silica and PDMS occured separately and simultaneously leading to the IPN.

The m-silica played a double role: cocuring with DGEBA and H-bonding with the oxygen atoms on the PDMS segments, and thus acted as a compatibilizer between DGEBA and PDMS and promoted the generation of the IPN structure and thus inhibited the curing-induced phase separation. The resulted partially miscible structure was characterized through the dispersion of silica particles and the glass transition behavior of the samples. This modification led to the enhancement of the mechanical properties of the nanocomposite based on DGEBA [138].

4.2. Preparation, properties and applications of nanocomposites from epoxy resins, silica, silicates and other nanofillers

Over the last twenty years nanotechnology has found many important applications, for example,
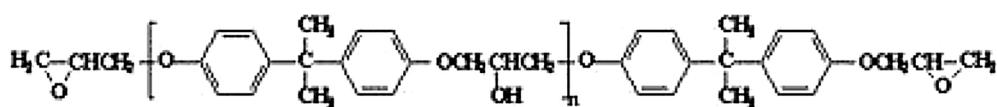
Diglycidyl ether of bisphenol-A, DGEBA type
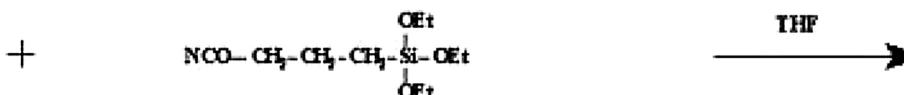
3-Isocyanatopropyltriethoxysilane
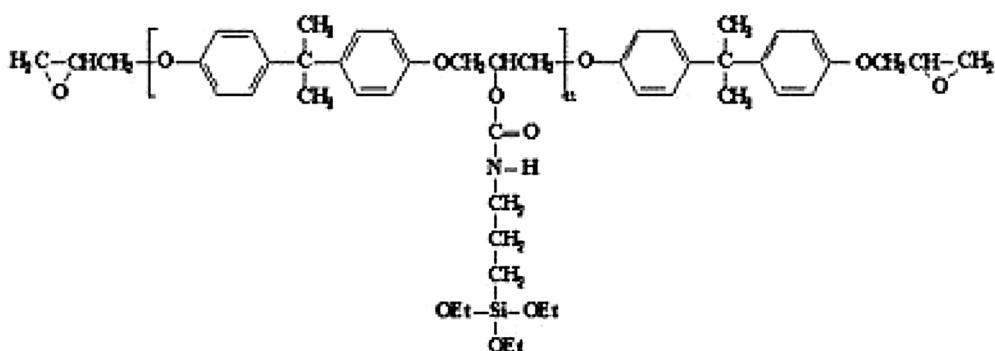
Scheme 32. The synthesis and structure of IPTES–epoxy. Reprinted (adapted) with permission from [137]. Copyright© 2007 Wiley Periodicals, Inc.

Isocyanuric Acid Triglycidyl Ester

3-Aminopropyltrimethoxysilane

Dimethyl acetamide, DMAc
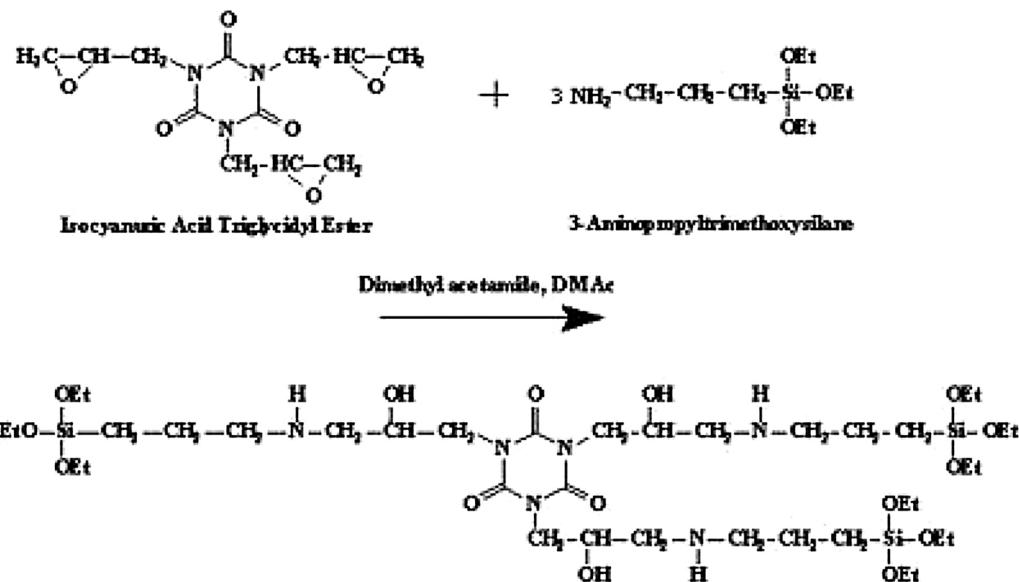
Scheme 33. The synthesis and structure of silane-modified isocyanuric acid triglycidyl ester (SM-IATE). Reprinted (adapted) with permission from [137]. Copyright© 2007 Wiley Periodicals, Inc.

in computing, sensors, and biomedical fields. The synthesis of nanoparticles of various materials and their complex architectures are major challenge of material scientists. Depending on the chemical structure and geometry there are three classes of nanoparticles:

1. layered materials, characterized by one nanometric dimension;
2. fibrous materials, characterized by elongated structures with two nanometric dimensions;
3. particulate materials, characterized by three nanometric dimensions.

Modified Epoxy

+

SM-IATE

H₂O/THF/H⁺
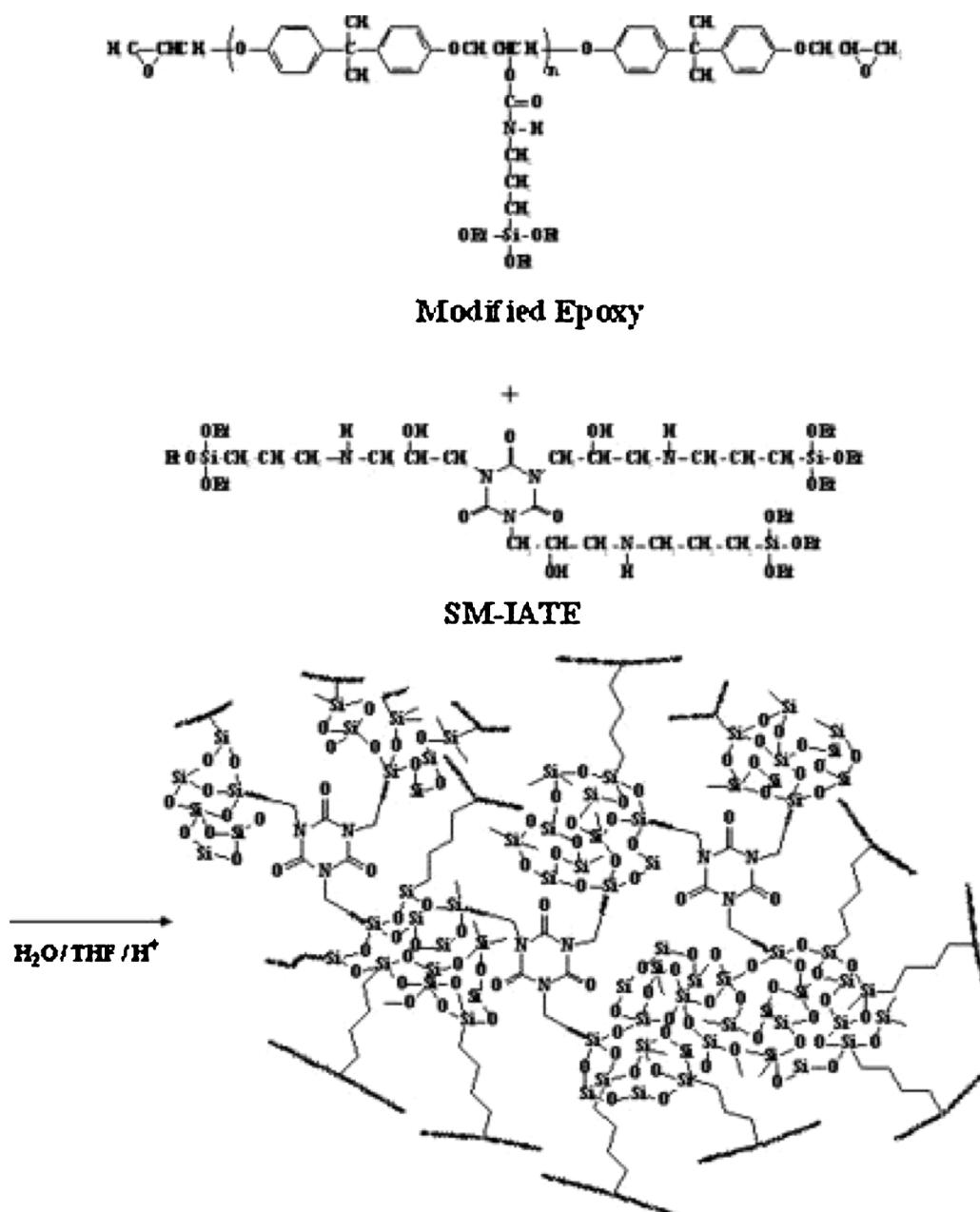
Scheme 34. The synthesis and structure of the IPTES–epoxy/silane-modified isocyanuric acid triglycidyl ester (IPTES–epoxy/SM-IATE) hybrid. Reprinted (adapted) with permission from [137]. Copyright© 2007 Wiley Periodicals, Inc.

One of the distinct advantages of nanocomposites over microcomposites lies in the performance improvement often acquired at relatively low concentration of nanofillers. Polymer nanocomposites have been applied in the automotive, aerospace, construction and electronic industries. Many of these materials are based on layered silicate compounds, e.g., montmorillonite [139].
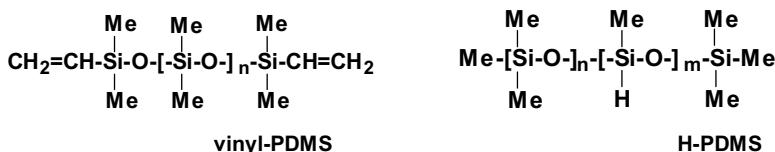
Fig. 15. The chemical structures of vinyl-PDMS and H-PDMS. Reprinted (adapted) with permission from [138]. Copyright 2007 Wiley Periodicals, Inc.
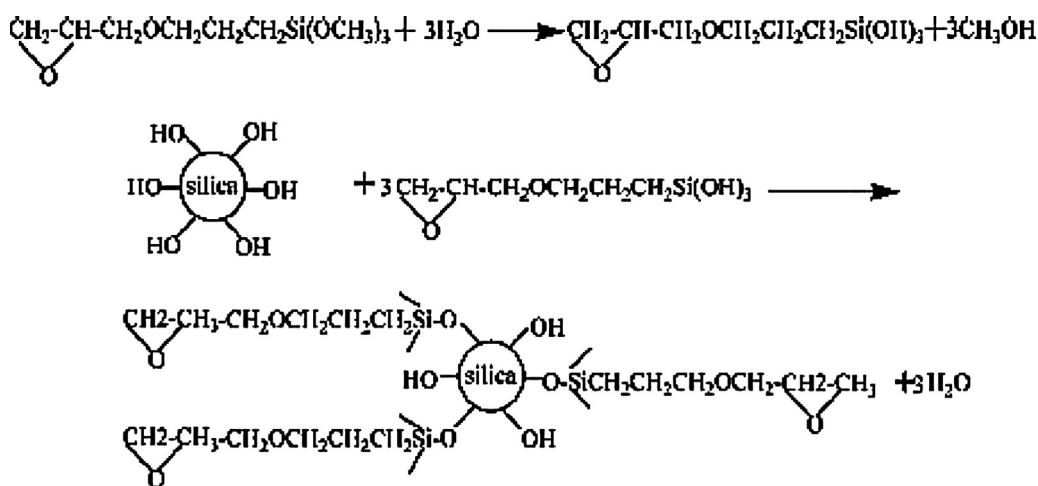
Scheme 35. The reaction Scheme of silica modification with epoxy groups. Reprinted (adapted) with permission from [138]. Copyright© 2007 Wiley Periodicals, Inc.

Polymer nanocomposites are now being more often used as sliding components, that were formerly composed only of metallic materials. They are utilized in tribological components such as cams, brakes, bearings and gears because of their self-lubrication properties, lower friction and better wear resistance. In 2006 the global nanocomposite market size was around 300 million US $ and was expected to exceed 1 billion US $ within the next 5 years [140].

Silica is the most widely used filler to improve the properties of epoxy resins. Reduction of the dimension of inorganic additives to nano-size scale is accompanied by increased difficulty of homogeneoua dispersion of the particles in the polymer matrix. Two approaches of the sol–gel process to prepare epoxy–silica hybrids may be noted:

(1) directly mixing epoxy resin with functional silanes, e.g., TEOS [141–145],
(2) introducing trialkoxysilyl groups into an organic elastomer with organofunctional silane prior to the sol–gel reactions [22,146–148].

Sun et al. [149] compared the effects of nanosized and microsized fillers in epoxy composites and found that the T_g was reduced, when the amount of nanofillers increased in epoxy nanocomposites, whereas that change did not occur in the corresponding microcomposites. Due to the strong tendency of nanofillers to agglomerate, their surface modification by organic agents is usually an effective way to afford possibilities for compatibility between nanoparticles and polymers.

Li modified an epoxy resin with two different kinds of silica (nano-SiO_2, standard SiO_2 particles with diameter 30–40 nm and 3 μm, respectively) and (3-glycidoxy-propyl)trimethoxysilane (GPTMS) [150]. FTIR spectra indicated that bonded stationary phase was formed with GPTMS between nano-SiO_2 and epoxy resin. The initial decomposition temperature T_d, impact strength and bulk resistivity of epoxy resin-based composite increased and then decreased after nano-SiO_2 content

reached 4 wt.%; optimal values were 323 °C, 89.2 kJ/m^2 and 3.56×10^{14} Ω cm, respectively. Similar behavior was observed with standard SiO_2/epoxy resin-based composites, optimal values were 308 °C, 17.13 kJ/m^2 and 2.80×10^{14} Ω cm, respectively. SEM analysis showed that the toughness of nano-SiO_2/epoxy resin-based composite and standard SiO_2/epoxy resin-based composite also increased and then decreased after nano-SiO_2 and standard SiO_2 content reached 4 wt.%. Modification role of nano-SiO_2 in epoxy resin-based composite was more effective than that of standard SiO_2 due to large specific surface area and active groups on surfaces of nano-SiO_2 particles. Similar behavior was shown for the toughness of epoxy resin-based composite with nano-SiO_2 and standard SiO_2 as showed the SEM images [150].

Transparent epoxy–silica–acrylate hybrid coating materials, based on the epoxy resin, (methacryloxypropyl)trimethoxysilane and tetraethoxysilane (TEOS) were prepared by radical solution copolymerization and the sol–gel process. (Aminopropyl)triethoxysilane (APTS) was used as the basic catalyst and curing agent. FTIR spectra indicated that organic and inorganic phases were linked by chemical bonds and that the hybrid materials had multiple functional groups: anhydride, epoxy, hydroxyl, carboxyl, and alkoxysilane groups that can form networks at room temperature. The hybrid materials had inorganic particle mean sizes of 36 nm and 45 nm for TEOS mass fraction 10% and 20%, respectively, with a homogeneous distribution of the particles in the polymeric matrix. With increasing TEOS content, the transmittance in the visible region of the hybrid materials and the *yellow index* (YI) decreased, while the absorbency at 300–400 nm, the onset decomposition temperature and maximum weight loss temperature increased. Both the degradation temperature at which drastic weight loss occurs (T_{max}) and the decomposition onset temperature (T_{onset}) increased with increase in the TEOS content [151].

Chang et al. [152] compared thermal, mechanical properties, moisture absorption and gas permeability of epoxy resin composites containing aminomodified silica
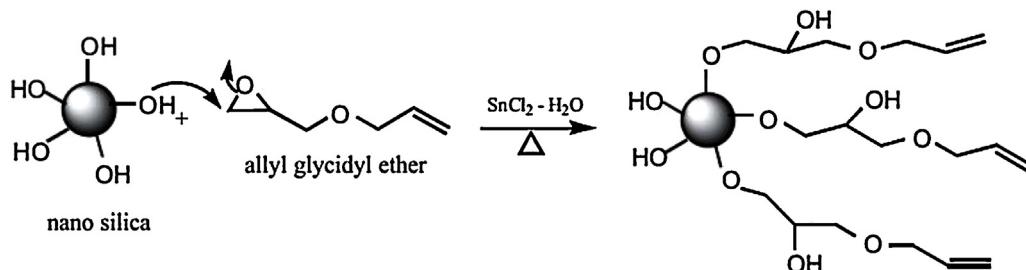
Scheme 36. A surface functionalization of nanosilica particles with allyl glycidyl ether. Reprinted (adapted) with permission from [154]. Copyright© 2005, Elsevier.

nanoparticles (AMS) or raw silica (RS) particles. The AMS nanofillers were synthesized by the conventional acid-catalyzed sol–gel reactions of tetraethoxysilane (TEOS), that acted as sol–gel precursor in the presence of amino-propyl(trimethoxy)silane (APTMS). Subsequently a series of hybrid materials was prepared by in situ thermal ring-opening polymerization reactions of the epoxy resin in the presence of AMS nanoparticles and RS particles. The AMS nanoparticles showed better dispersion capability in the polymer matrices than in case of RS particles.

Epoxy–AMS nanocomposites exhibited enhanced thermal and mechanical properties and reduced moisture absorption and gas permeability. The surface of the nanosilica particles was chemically modified with allyl glycidyl ether. Nanosilica functionalized with allyl ether and hydroxyl groups (see Scheme 36) was applied for the modification of the properties of epoxy resins and other polymeric materials [153,154].

Wang and coworkers [155] prepared a heat-resistant epoxy–silica hybrid material based on DGEBA epoxy resin filled with various amount of GPTMS and silica nanoparticles, cured with 4,4′-diaminodiphenyl sulfone (DDS). The addition of GPTMS not only improved the compatibility between silica and the epoxy matrix, but also increased the crosslinking density of the epoxy system, meanwhile the nanosilica further reinforced the inorganic network of the hybrid material. Consequently, the nanocomposite showed much improved heat-resistant properties. The storage modulus of the hybrid systems showed a high value of the glass transition – up to 300 °C. The integral thermal stability of the resulting materials was also improved as compared to the neat epoxy resin. The mesoporous surfaces of tetramethoxysilane (TMOS)-derived silica aerogels were modified with amines by copolymerization of TMOS

with (aminopropyl)triethoxysilane (APTES). In this system an amine functionality was introduced into silica aerogels by copolymerization and gelation of TMOS and APTES in up to 1:1 volume ratios.

The resulting gels were further treated with di-, tri-, or tetrafunctional epoxy monomers (see Fig. 16) in various concentrations [156]. The epoxy cross-linked aerogels appeared more elastic and retained higher porosity than their isocyanate modified silicas. The trifunctional epoxide yielded the strongest cross-linked aerogels mainly due to its increased reactivity over the bifunctional and tetrafunctional epoxides. Maximum strength was attained neither at the maximum density nor at the highest concentration of −NH$_2$ groups, suggesting surface saturation effects. Therefore, the most favorable combination of −NH$_2$ group concentration with optimal exposure to epoxide for maximum cross-linking was identified. The dried aerogels were heated at ∼150 °C in order to complete curing reactions of residual unreacted epoxy groups. It was concluded that this post-curing process could be responsible for further strength increase and decreased cure time [156].

Spherical silica powders (SSP), with their low coefficient of thermal expansion (CTE) and high fluidity, are used to strengthen resins, especially in semiconductor encapsulates. Jin et al. [157] prepared SSPs by an oxygen–acetylene flame method and obtained composites of the spherical silica and the epoxy resin by a stepwise thermal curing process, with tetrahydrophtalic anhydride as the curing agent and 2,4,6-tri(dimethyl-aminemethyl)phenol as an accelerator. The effects of SSP on mechanical properties, CTE, thermal stability and thermal degradation behavior of epoxy–silica nanocomposites were studied. The initial decomposition temperature and mechanical properties increased significantly after adding spherical silica to the
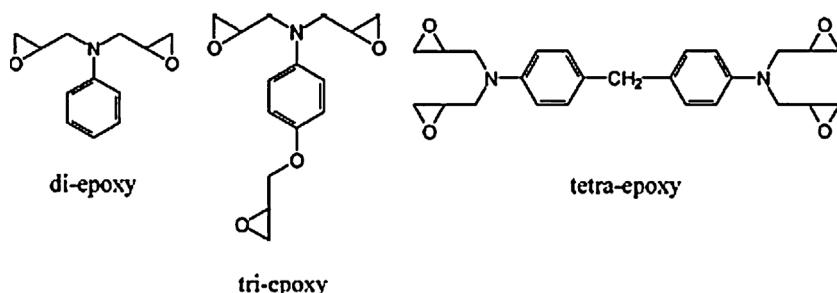
Fig. 16. The structures of multifunctional epoxy monomers. Reprinted (adapted) with permission from [156]. Copyright (2005) American Chemical Society.

composite. The maximum properties of thermal stability and mechanical properties were observed with 30% of volume fraction of fillers in the system, and the thermal expansion was significantly reduced.

The organic–inorganic hybrid interpenetrating network (IPN) was obtained from DGEBA, poly(oxypropylene)diamine (D 2000), and TEOS [158]. The sol–gel hydrolytic condensation of TEOS was catalyzed with *p*-toluenesulfonic acid monohydrate (TSA). The inorganic phase caused reinforcement of the rubbery material. Grafting of silica–siloxane structures on the epoxy network was possible by condensation reactions of Si—OH groups with the C—OH groups, that formed during reaction of epoxy groups with amines. The formation of silica from TEOS during the sol–gel process was confirmed by ^{29}Si NMR spectroscopy, gas chromatography, electron microscopy, and small-angle X-ray scattering. Large aggregates of silica (100–300 nm in diameter) were formed during the one-stage polycondensation. In a two-stage process with the acid prehydrolysis of TEOS faster gelation and formation of smaller silica particles (50–100 nm in diameter) were observed. The most homogeneous hybrid morphology, with the smallest silica nanoparticles (10–20 nm in size) appeared, when a two-stage sequential synthetic procedure was applied. These results showed that the presence of organic epoxide–amine reagents controlled the growth of the silica structure in the IPN hybrid (DGEBA–D2000–TEOS). Poly(oxypropylene)diamine affected the polycondensation reaction of TEOS and morphology of the cured resins. The D2000 was not effective in catalysis of TEOS hydrolysis but it substantially accelerated gelation process. The poly(oxypropylene) chain of D2000 ensured a good solubilization of the silica leading to transparent gels, that formed during TEOS polycondensation, in contrast to the base catalyzed process, e.g., by benzyldimethylamine (BDMA) [158]. Moreover, in the two-stage process a much faster gelation of the silica was observed. The silica network formed faster than the epoxy matrix, and its structure was not affected by the presence of the epoxide component. In the case of the sequential procedure, the preformed epoxy network suppressed growth of the silica aggregates via homocondensation reactions of Si—OH groups from silica nanoparticles, and the relatively small silica particles were formed [158].

The morphology and properties of hybrid polymers are dependent on the size, nature and strength of the interface, that are easily achieved in the sol–gel process [146,159–162]. It was concluded that amine-cured epoxy–silica composites have better compatibility as a result of stronger physical interactions through hydrogen bonds between amino groups and siloxane linkages [11,12]. The coupling agents and other chemicals used significantly improved compatibility through covalent chemical binding the organic and inorganic ingredients [17,160].

Several epoxy–silica hybrids were synthesized from DGEBA, TMOS and GPTMS with tetraethylenepentamine (TEPA) or benzyl(*N*,*N*-dimethyl)amine (BDMA) as curing agents. In the hybrid systems cured with TEPA, the thermal and mechanical properties of the epoxy resin were significantly improved by addition of small amounts of TMOS. However, this phenomenon was not observed in the hybrid systems cured with BDMA. In the hybrid systems cured with TEPA, the FTIR results showed the formation of a covalent bond between the silanol and hydroxyl groups, generated by the hydrolysis of the alkoxysilane groups and the reaction of the epoxy group with an active hydrogen of TEPA. Based on TEM observations the hybrids cured with TEPA showed a homogeneous microstructure in contrast to the hybrids cured with BDMA. Thus, the difference in the interfacial interaction between the organic and inorganic phases, caused by differences in the network structures of the organic matrices, affect the properties and microstructures of epoxy–silica hybrids [160].

Other organic–inorganic IPNs were synthesized with an organic phase made of the epoxy resin and the silica phase by sol–gel chemistry [163] from TEOS, in the presence of the epoxy resin [164]. TEOS was converted to SiO$_2$. The two types of polymerization used were sequential and simultaneous with SiO$_2$ content ranging from 0.02 to 0.43 g SiO$_2$/g total weight. The morphologies of products were examined by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) and showed strong phase separation for samples made with sequential polymerization methods, and extensive phase mixing for samples made by simultaneous polymerization methods. The sequential IPNs were strongly phase separated into finely divided SiO$_2$ phase of ~10 nm in size. The simultaneous IPNs were weakly phase separated, with considerable mixing in the phases. With M_c = 2000 g/mol of polypropyleneglycol diamine hardener, the characteristic size of the SiO$_2$ domains increased slightly, when the SiO$_2$ content was increased. However, the particle size was not strongly correlated with the crosslink density in the epoxy phase. It is quite obvious that sol–gel chemistry is capable of producing unique morphologies that are not possible through simple physical mixing. In addition, the morphologies are of a nano-scale size and may be continuous or interconnected, with a major influence on macroscopic properties such as thermal stability and mechanical properties [164].

Thermal studies showed increased thermal stability for the IPNs, compared with unfilled epoxies or physically mixed silica filled epoxy resins. The thermal stability of epoxies was unchanged when 0.10 g SiO$_2$/g total weight was physically mixed with epoxy monomers and cured. When a similar content of SiO$_2$ was formed chemically by a sequential or simultaneous polymerization, the thermal stability was enhanced, leading to higher degradation temperatures, lower rates of weight loss and higher char yield. The pyrolyzed skeleton of the epoxy–SiO$_2$ IPN from the TGA experiments suggested that the silica phase was continuous in the IPN, even though it was the minor phase [164].

A series of ultraviolet-curable hybrid materials were synthesized by a sol–gel process based on TEOS and polyurethane acrylate–epoxy acrylate resin. 3-(Trimethoxysilyl) propyl methacrylate was used as a second inorganic substrate and the silane coupling agent in order to improve the compatibility between the organic polymer and inorganic materials. Nearly uniform dispersion of SiO$_2$ particles with the diameters ~100 nm were observed by field emission SEM. The surface morphology was scanned

by atomic force microscopy (AFM). The results of TGA showed that the hybrid material performed desirable optimal thermal stability and uniform microstructure, for a mass ratio of TEOS to polymer components was 0.4:1. This composite was suitable for optical fiber coating in high temperature application [165].

Organic–inorganic hybrids with 1 to 7 wt.% silica contents were synthesized from bisphenol-A and epichlorohydrin, modified with 3-thiopropyltriethoxysilane (TPTES). The reactive coupling agent TPTES was introduced to the epoxy resin to obtain high adhesive strength material for engineering industry. It was expected that after hydrolysis the multiple reactive functional silanol groups Si—OH of TPTES can react with the epoxy resin to increase the shear strength and toughness of the epoxy resin. IR spectra indicated that bonded stationary phase was formed. The introduction of TPTES into epoxy resin had crucial effects on the fracture surfaces and mechanical properties of composites. Both the shear strength and elongation of epoxy resin-based composites increased and then decreased, when SiO_2 content reached 5 wt.%, and optimal value was 24.8 MPa. Existence of particles had influence on the morphological structure of composites, that in turn affected the shear strength and the toughness of the composites [166].

Hybrids of the epoxy resin with silica were prepared by curing the resin with methyl-5-norbornene-2,3-dicarboxylic anhydride (methyl nadic anhydride, MNA), in conjunction with BDMA as catalyst, and DDS, respectively. Number average molecular weights of the epoxy resin were 370, 880 and 5000 g/mol, that correspond to an average degree of polymerisation of 0.1, 2 and 16, respectively. Control of the morphology was achieved through functionalization of the DGEBA resin with monofunctional (N-phenylaminopropyl)(trimethoxy)silane or difunctional secondary amine trialkoxysilane: bis(3-trimethoxysilylpropyl)amine, prior to being mixed with a solution of TEOS and the hardener (DDS). The results of SEM and TEM studies showed that the preparation conditions and the solvent played a crucial role in the compatibilization of the final hybrid and affected the morphology of the composites samples. The addition of the hydrolyzsed TEOS solution into the epoxy resin to produce the corresponding hybrid was found to interfere with the cross-linking reactions with the hardener, resulting in a reduction in the T_g of the epoxy resin component. This could be caused by side reactions of MNA with the ethanol formed from hydrolysis and condensation of TEOS, producing monofunctional and difunctional esters that acted as plasticizers and to decreased functionality of the epoxy resin from the reaction with the HCl used for the hydrolysis of TEOS [167].

Secondary aliphatic aminosilanes were more effective than aromatic/aliphatic aminosilanes for the compatibilization of epoxy resin-silica hybrids. The level of compatibilization achievable for such hybrids can be enhanced by increasing the following parameters: (a) molecular weight of the resin, (b) degree of functionalization of the epoxy resin, (c) polarity of the solvent and (d) processing temperature. The glass transition temperature of the epoxy network in a ceramer was lower than
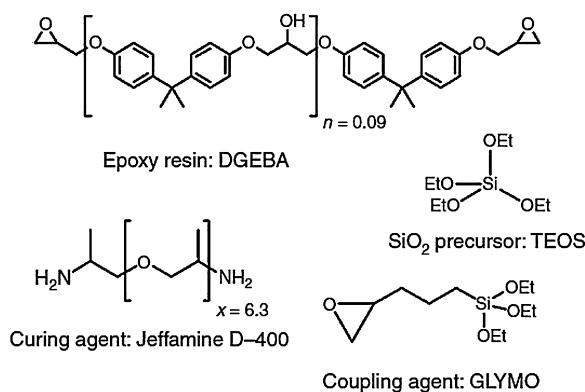
Fig. 17. The molecular structures of the substrates used in preparation of epoxy–silica nanocomposites. Reprinted (adapted) with permission from [169]. Copyright 2013, Springer Science + Business Media B.V.

the value obtained in the absence of the inorganic phase [167].

The epoxy–silica hybrids containing molybdate anions as dopants for the siloxane domains were prepared from a silane-functionalized resin mixture of two DGEBA oligomers with different molecular weights. The functionalization of the epoxy resin was carried out using aminopropyl- and mercaptopropyltrimethoxysilane, respectively. The molybdate anions were added as "bound" species in the form of salts produced from prereactions with a fractional amount of the cycloaliphatic amine hardener, and as "free" molybdic acid. The co-continuous silica domains within the epoxy networks were prepared by the incorporation of pre-hydrolysed mixtures of TEOS and (3-glycidoxyl)(trimethoxy)silane (GLYMO) into the precursor solution used for the preparation of epoxy–silica hybrids. The addition of a source of molybdate anions to the hybrid precursor solution led to the formation of a dense siloxane network and to the substantial increase in the T_g of the organic phase [168].

The effect of silica content and its organic compatibility on the thermal properties of epoxy–based nanocomposites (NCs) has been investigated quite often. Bicontinuous epoxy–silica nano-composites were synthesized in situ using two-stage polymerization of silanes and epoxy monomers (Fig. 17)—solventless hydrolysis of TEOS took place inside of the liquid epoxy resin, followed by the crosslinking of epoxide moieties with a diamine curing agent [169]. Two kinds of epoxy-silica nanocomposites containing 0–30 wt.% silica, were prepared in that way:

(1) EpSi-A nanocomposites—from epoxy–amine and tetraethoxysilane (TEOS), having only physical interfacial connections, e.g., hydrogen bonds, and
(2) EpSi-B nanocomposites—from epoxy–amine, TEOS, and an epoxy–silane coupling agent (GPTMS), having both physical and chemical linkages at the interface of epoxy and silica phases.

The epoxy–silane coupling agent GPTMS was applied to improve the organic compatibility of silica in EpSi-B nanocomposites. The amount of GPTMS was adjusted

so that only 5 wt.% of the total silica content in EpSi-B nanocomposites was derived from GPTMS. The composites synthesized via two-stage polymerization were characterized by FTIR spectro-scopy, differential scanning calorimetry (DSC), and thermogravimetric (TG) analysis. DSC and TG/DTA results revealed substantially high glass transition T_g and excellent thermal stability of the bicontinuous NCs, as compared with pristine epoxy polymer. Both T_g and thermal properties, however, considerably varied, depending on the organic compatibility of the NCs. Significantly higher decomposition temperatures were recorded with EpSi-B nanocomposites owing to the chemical links between the epoxy and silica phases [169].

In similar studies carried out by Afzal and Siddiqi [16], epoxy–silica hybrid polymers were obtained as thin free-standing films. ES-A hybrid polymers were formed from epoxy–amine, and TEOS, ES-B hybrid polymers—from epoxy–amine, TEOS, and GPTMS. Small-sized silica networks were formed in the sol–gel process, well-distributed in the organic matrix. The formation of phase bicontinuous hybrids was possible due to the interactions of hydroxyl groups of nanosilica with the epoxide. The addition of GPTMS substantially affected the particle size and distribution of silica, the interface interactions through chemical crosslinks between the organic and inorganic components, improved the adhesion of the two phases, inhibited the macroscopic phase separation, and enhanced bicontinuity of the phases [15]. In the proposed structure of ES-A hybrids, presented in Fig. 18, only hydrogen bonds are shown, while the two ingredients are also connected through covalent bonds. On this base the phase bicontinuous structure in ES-B hybrids was suggested. Although, physical crosslinks such as hydrogen bonding contributed toward improved dispersion of silica, the aggregation of silica nanoparticles took place at higher contents (>15 wt.%) and caused the phase separation. Addition of GPTMS resulted in better mixing of the substrates at the molecular level and in increased homogeneity within the polymer film [16].

The glass transition temperatures, thermal stability, and rate of mass loss of the pristine epoxy polymer were improved with the introduction of silica into epoxy networks. Both T_g and thermal properties, however, considerably varied depending on the organic compatibility of the nanocomposites. The T_gs of epoxy–silica hybrids were also significantly increased in comparison with a pristine epoxy resin and reached a maximum of 13.6% and 20.4%, for samples containing 10 wt.% of silica, and had following values: for ES-A ($T_g \sim 50\,°C$) and for ES-B ($T_g \sim 53\,°C$), respectively, attributed to the formation of interpenetrating epoxy–silica networks. The activation energies of the nanocomposites and the char residues also increased with the silica content [16].

The results of GCMS and DSC analyses indicated that it was possible to reach complete conversion of silanes and epoxy groups. These epoxy–silica films were characterized by the ATR FTIR spectroscopy and AFM. The AFM micrographs showed a very fine dispersion of nanosilica into the organic matrix, improved by addition of GPTMS. The coupling agents can significantly improve compatibility through covalent chemical links between the organic and inorganic components [16]. The epoxy––silica hybrids are novel materials useful for stone conservation, suppressing water penetration into the stone. The protective treatment goal is the preservation of the "skin" of the stone against the rainwater, gaseous pollutants, solid particulate, and thermal stress. As a consequence the main purpose of the protection of facades against water intrusion involves the coating of the stone surfaces with low surface energy materials and epoxy–silica hybrids were employed in stone coating [170,171]. The introduction of fluorine atoms into these hybrid materials enhances hydrophobicity, chemical inertness, and weathering resistance [172,173]. Cardiano [174] described epoxy–silica coatings, prepared from DGEBA, APTMS, GPTMS, and two fluorine-containing comonomers with oxirane ring and trimethoxysilane groups. The reaction of the aminosilane with the epoxy DGEBA and GPTMS led to visually transparent, crack-free and insoluble solids with hydrophobic properties modified with two fluorine-containing additives. It is commonly known, that the receding contact angle of an ideal hydrophobic agent should not be less than 90°. The presence of fluorinated species induced a significant increase of the receding angle to 100°. The
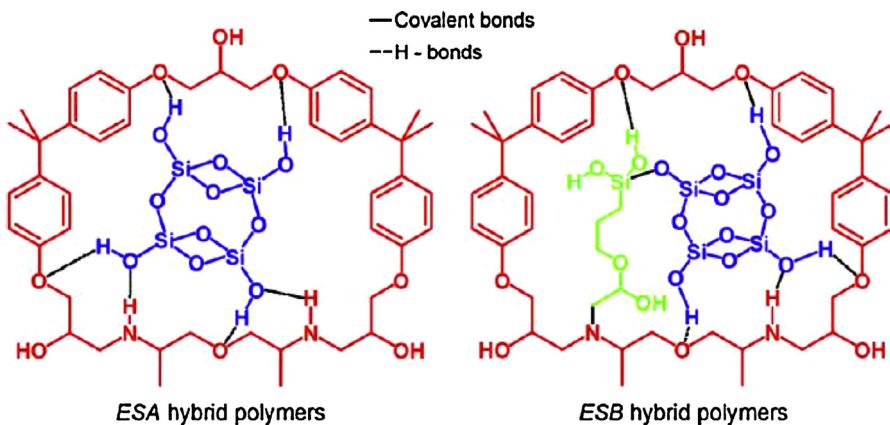
Fig. 18. The proposed structures and interactions in the two kinds of epoxy–silica hybrid polymers. Reprinted (adapted) with permission from [16]. Copyright 2011, Elsevier.
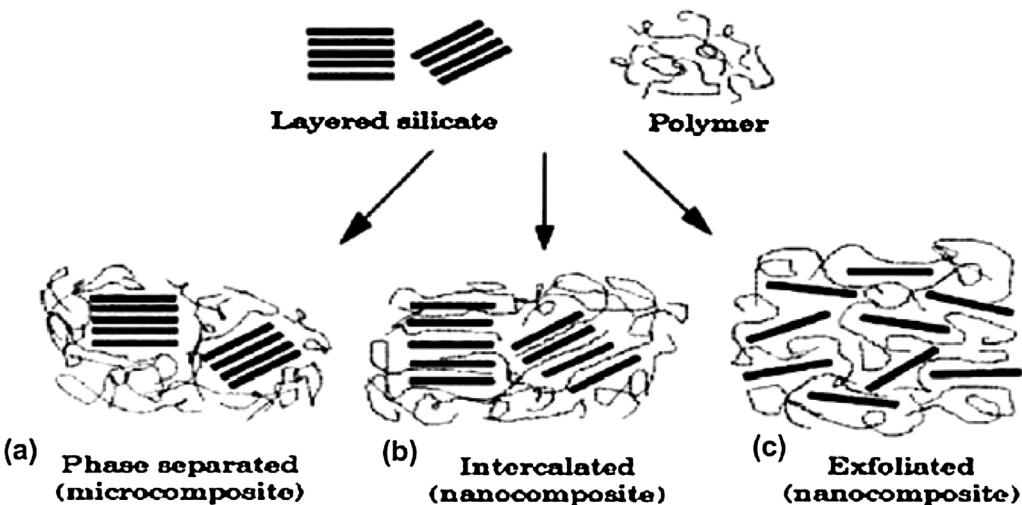
Fig. 19. Schematic illustrations of different structures of composite of layered silicates and polymers: (a) phase separated microcomposite, (b) intercalated nanocomposite, and (c) exfoliated nanocomposite. Reprinted (adapted) with permission from [179]. Copyright 2011, Elsevier.

mixture with DGEBA, APTMS and fluorinated trimethoxysilane comonomer represented the most effective barrier to impart strong hydrophobicity to the coated surface.

Nano-sized Al_2O_3 particles were used as fillers in polymeric composites for improving the tribological performances. Alumina is famous for its hardness and is often used as a grinding medium. It is not a suitable filler in the microscale particulate form due to its angularity, but this material in nanoscale particulate form has much lower angularity and thus is not abrasive. Kishore and Kumar [175] found that the addition of alumina powder of the size ≤1 μm into epoxy resin increases the sliding wear resistance of material. Shi et al. [176] compared the friction and wear properties of differently treated nano-Al_2O_3/epoxy composites. In order to enhance the interfacial interaction between fillers and epoxy matrix the nanoparticles were pretreated by either APTES or graft polymerization with the monomers of acrylamide, styrene and ethyl acrylate, respectively. The experimental results indicated that the frictional coefficient and wear rate of the epoxy resin were reduced at rather low concentration of nano-Al_2O_3. The lowest specific wear rate was observed for the composites with 0.24 vol.% nano-Al_2O_3 grafted by polyacrylamide. Although the incorporation of nanofillers led to increased flexural modulus and flexural strength of the epoxy resin, the wear performance of the composites did not correlate with the static mechanical properties.

Aluminum-polymer composites are attractive materials for many industrial applications due to their low density, corrosion resistance, thermal stability and ease of fabrication. Rhee and coworkers [177] showed that the modification of an aluminum filler with APTES improved the tensile modulus and strength, as well as the fracture toughness and wear resistance of aluminum-epoxide composites. The authors attributed these enhanced properties to the improved dispersion and bonding of aluminum particles in the epoxy resin, due to the silylation of a filler powder. The good dispersion and interfacial strength between aluminum powder and polymer are

the main issues in the fabrication of aluminum-polymer composites.

Special nanocomposites were obtained by mixing epoxy resins with layered silicates (nanoclays). The most often used layered silicates is montmorillonite (MMT) [178]. This material comprising sheet-like platelets, that are about 1 nm in thickness and 100–1000 nm in width and length, so they possess high aspect ratios and large surface area. The high aspect ratio of the clay platelets permit significant reinforcement at relatively low loading if the high degree of exfoliation or intercalation is achieved.

The dispersion of clay tactoids in polymer matrix can result in the formation of three types of composites (Fig. 19):

(1) conventional microcomposites, that contain clay tactoids dispersed simply as a segregated phase;
(2) intercalated polymers–clay nanocomposites, that are formed by the infiltration of one or more molecular layers of polymer into the clay host galleries;
(3) exfoliated polymer–clay nanocomposites as characterized by low clay content, a monolithic structure, with separation between clay layers.

Exfoliation is particularly desirable for improving specific properties that are affected by the degree of dispersion and the resulting interfacial area between polymer and clay nanolayers. The hydrophilic nature of the clay leads to incompatibility with most of hydrophobic polymers. Thus, a modification of the clay or polymer resin or both has been carried out to enhance the interaction between the clay and the polymer. The surface of the MMT is commonly modified with cation exchange technique in order to make layered silicate compatible with most hydrophobic polymers.

The use of a silane coupling agent is the second method for surface modification of nanoclay. Pinnavaia and coworkers [180,181] studied the effect of organo-surfactant chain length on the delamination of epoxy–clay nanocomposites and they found that tensile strength

n = 0 (88 %), n = 1 (10 %), n = 2 (2 %)
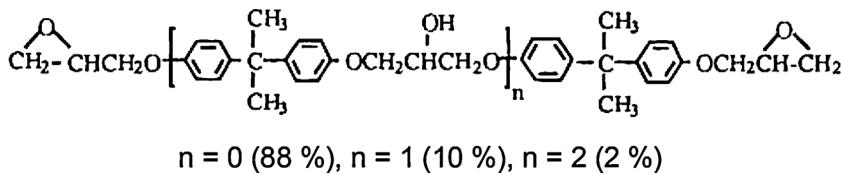
Fig. 20. The structure of the epoxy resin used for the preparation of the epoxy–magadiite hybrid composite. Reprinted (adapted) with permission from [185]. Copyright (1998) American Chemical Society.

and Young's modulus increased with the increment of organo-surfactant chain length and the loading content. Organo-modified montmorillonite (OMMT) nanofillers play an important role to improve the wear resistance of polymer composites. Renukappa and coworkers [179] described that the inclusion of 5 wt.% of OMMT, surface treated with octadecylamine surfactant, increased the wear resistance of epoxy nanocomposite significantly.

Hydrophilic fumed silica-clay nanocomposites, prepared from DGEBA resin, filled with fumed nanosilica (FS) and montmorillonite (MMT) and cured by TETA were studied by Kumar et al. [182]. The surfaces of both nanofillers were chemically modified with APTMS. The addition of modified FS into the epoxy resin affected the curing behavior, enhanced thermal stability and improved tensile and impact properties over neat epoxy polymer and the epoxy composite containing the second filler. Moreover, nanocomposites with modified MMT showed ductile nature in comparison with brittle pure epoxy system.

The key factor responsible for the enhancement of the tensile and impact strength, the stiffness modulus and the fracture toughness of the epoxy resins filled by nanoclay is the degree of exfoliation of the filler into the epoxy matrix [183]. Complete exfoliation of MMT, modified with APTMS, was observed in the epoxy composites reinforced with glass fiber (GF) and OMMT, prepared with the hand-lay-up technique [184]. These composites showed improved flexural modulus and strength, and better interfacial interaction and wettability between the epoxy matrix and the glass fiber.

The epoxide resin (DGEBA) with MW $\sim$ 377 (see Fig. 20) was used for the formation the epoxy–magadiite hybrid composite [185], cured with poly(propylene glycol) bis(2-aminopropyl ether) of MW $\sim$ 2000 g/mol. A rubber-like epoxy polymer matrix with T_g of $-40\,^\circ$C was obtained. Paraffin-like organomagadiite intercalates, interlayered by primary, secondary, tertiary, and quaternary onium ions, were used to form elastomeric polymer-layered silicate nanocomposites by in situ polymerization during the thermoset process. Depending on the nature of the onium ions, intercalated or the exfoliated magadiite nanocomposites were obtained.

The exfoliated NCs were typically disordered, but a new type of exfoliated structure also was observed in which the nanolayers were regularly spaced over long distances (e.g., $\sim$80 Å Bragg spacings). The tensile properties of the polymer matrix were improved greatly by the reinforcement effect of the silicate nanolayers. Exfoliated silicate nanolayers were more effective than intercalated assemblies of nanolayers in optimizing reinforcement. Exfoliation

of organomagadiite in the rubbery epoxy matrix improved the elongation at break, while improving tensile strength, that is opposite to the behavior of the conventional composites.

Lu et al. [186] reported that the exfoliating ability of the organoclays in the epoxy resin is also dependent on the nature of the curing agent used. Chin et al. [187] found that for the m-phenylene diamine (MPDA) cured epoxy systems, exfoliated nanocomposites were formed with epoxy cured with less than an equimolar concentration of MPDA or with homopolymerization of the epoxy without a curing agent, whereas the intercalated structure was only observed with a large excess of the curing agent. Hutchinson and coworkers [188] also studied the influence of homopolymerization reaction of epoxy resin on the degree of exfoliation of layered silicates.

Modification of MMT with a traditional modifier, such as a long-chain alkylammonium derivative, is a physical modification, and cannot provide the chemical interaction between polymer and MMT that can induce high mechanical properties, such as tensile strength and toughness. The use of silane coupling agents made possible the chemical modification of nanoclays. Ryu and coworkers [189] used MMT functionalized with (3-aminopropyl)triethoxysilane (APTS) for preparation of MMT–epoxy nanocomposites. They found that the tensile strength and elongation at break of the studied NCs improved significantly by the silane functionalization of nanoclays. (3-Aminopropyl)trimethoxysilane (APTMS) was applied by He and coworkers [190] for the chemical modification of the clay surface, with acetone as an unreactive solvent to facilitate clay modification and dispersion. Improvements of storage modulus, Young's modulus and fracture toughness were observed with incorporation of 1–3 wt.% silane-modified clay in MMT–epoxy nanocomposites. However, clay minerals have poor the electrical and thermal conductivity. In order to improve these properties, carbon-based nanofillers were introduced to the polymer–clay nanocomposites. Four types of carbon nanofillers may be applied for this purpose:

(1) graphene,
(2) graphite,
(3) carbon nanotubes (CNTs) and carbon nanofibers (CNFs).
(4) fullerenes (C60).

A comparison of the mechanical, thermal and electrical properties of graphene with CNTs, steel, plastic, rubber and fiber is presented in Table 1 [191]. The tensile strength of graphene is close to CNTs, and much higher than that

Table 1

Properties of graphene, CNT, nano sized steel, and chosen polymers. Reprinted (adapted) with permission [191]. Copyright© 2010, Elsevier.

Materials	Tensile strength	Thermal conductivity at room temperature [W/m K]	Electrical conductivity [S/m]
Graphene	130 ± 10 GPa	$(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$	7200
CNT	60–150 GPa	3500	3000–4000
Steel NPs	1769 MPa	5–6	1.35×10^6
HDPE	18–20 MPa	0.46–0.52	Insulator
Natural rubber	20–30 MPa	0.13–0.14	Insulator
Kevlar (fiber)	3620 MPa	0.04	Insulator

of other nanofillers. The thermal conductivity of graphene is higher than all these materials, and the electrical conductivity of graphene is also higher than the other organic materials. Because of exceptional mechanical properties and thermal and electrical conductivity CNTs and CNFs are ideal reinforcing agents for functional polymers.

Due to lower manufacture cost, CNFs have a better chance in large-volume industrial application than CNTs, although both carbon nanofillers have been used in preparation of the epoxy nanocomposites. Good dispersion of CNTs and CNFs in a polymer matrix is the greatest challenge for reinforcing epoxy composites. Considerable research has been carried out to improve the dispersion of nanofillers in the polymer matrix and to enhance the interaction of CNTs or CNFs with the matrix by using high-shear mixing, ultrasonication and wrapping polymers or other surfactants on the surface of nanofillers. These methods can facilitate good dispersion of nanofillers, but the weak physical interaction permit the fillers to easily pull out from the matrix.

The chemical modification is another way for increasing the interfacial force between the matrix and the fillers through covalent bonding. Generally the oxidation process is the first step in modification of carbon nanofillers and the silanization enables effective modification for CNTs and CNFs to tailor the electrical properties and thermal conductivity of CNT–epoxy systems or CNF–epoxy nanocomposites for the attachment in the integrated circuit packaging industry. Zhu et al. [192] reported on the investigation of the rheological and electrical conductive behavior of epoxy resin nanocomposite suspensions with CNFs. Oxidized in concentrated nitric acid, CNFs reacted with (3-aminopropyl)triethoxysilane (APTES). Reaction between the amine-terminated functional groups on the surface of CNFs and the epoxy resin was carried out in situ and was responsible for the improved fiber dispersion and network formation.

Nie and Hubert [193] modified CNFs in a multistage process including oxidation, reduction and silanization. CNFs were first oxidized by a mixture of concentrated H_2SO_4 and HNO_3 to form carboxyl groups on the fiber surface. The silanization reaction is carried out between carboxyl groups on the CNF surface and alkoxysilane at high temperature, but the spatial hindrance of carbonyl groups lowers its efficiency:

$$CNF\text{—}COOH + RO\text{–}Si \equiv \rightarrow CNF\text{—}CO\text{—}O\text{—}Si \equiv + ROH \quad (4)$$

Nie and Hubert reduced the carboxyl groups to alcohol groups (Eq. (5)) to improve the reaction activity and accelerate the reaction.

$$CNF - COOH \xrightarrow[\text{THF}]{\text{NaBH}_4/\text{I}_2} CNF - CH_2 - OH \quad (5)$$
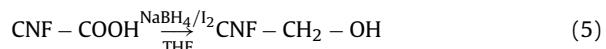
Finally the hydroxyl groups on the surface of CNFs were reacted with APTMS:

$$CNF\text{-}CH_2OH + (CH_3O)_3Si(CH_2)_3NH_2$$

$$\rightarrow CNF\text{—}CH_2\text{—}O\text{—}Si(OCH_3)_2(CH_2)_3NH_2 + CH_3OH \quad (6)$$
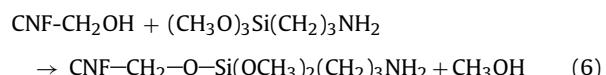
Silanized CNFs were incorporated into the epoxy resin by solution processing and epoxy composites obtained by further curing. The studies indicated better dispersion of modified fibers in the epoxy matrix, improved mechanical and thermal properties of composites and reduced electrical conductivity. Silanized 3-D carbon fibers were used by Xu et al. [194] to reinforce hydroxyapatite-thermosetting epoxy composite. These bioactive ceramic-polymer composites were developed by analogy to bone.

Silicon carbide (SiC) was also found to be good filler for epoxy composites. SiC forms two types of crystal structures, i.e., α-SiC of hexagonal structure and β-SiC of face-center-cubic structure with the better mechanical properties than that of the former. The excellent properties of β-SiC (high strength and modulus, high temperature and corrosion resistance, and thermal shock and wear resistance) have been very useful in the preparation of high-performance composites. For good interactions of SiC and polymer matrix the surface modification of silicon carbide was necessary. Gu et al. [195] used GPTMS, that formed a layer of single molecular membrane on the surface of β-SiC and improved their wettability and dispersion in the epoxy resin. The SiC–epoxy composites were obtained by blending-casting molding method. Both flexural strength and impact strength of the composites increased with the increasing of SiC content, but decreased with excessive addition of SiC, and the maximum of mechanical properties was observed at 10 wt.% of SiC content.

4.3. Nanocomposites of epoxy resins with POSS

Polyhedral oligomeric silsesquioxane (**POSS**) is the most attractive of a new class of well-defined nanofillers, that have been developed over the last twenty years. The POSS exhibits the nanosized cage architecture composed of Si–O–Si framework with empirical formula
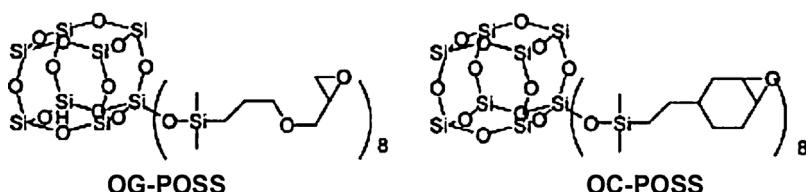
Fig. 21. The chemical structures of OG–POSS and OC–POSS. Reprinted (adapted) with permission from [105]. Copyright 2001 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

$(RSiO_{1.5})_n$ (n = 4, 6, 8, ...); R is generally an organic substituent: methyl, phenyl, vinyl, halogen, hydrogen, or other [58,60]. Among nanofillers, octasilsesquioxanes (denoted T_8) attract more attention because of their unique cubic-like structure. In contrast to clay or conventional fillers, POSS has the advantages of a monodisperse molecular weight with a well-defined structure, low density, high-temperature stability, no trace of metals and sizeable interfacial interactions between composite particles and polymer segments. The incorporation of POSS into a polymer provides simplicity in processing and the excellent comprehensive properties of this class of hybrid materials, such as mechanical properties, thermal stability, reduced flammability, and increased gas permeability. The enhanced properties include also lower thermal expansion, lower dielectric permittivity, and lower surface energy. The POSS cage can act in the polymer either as the reinforcing filler or as the plasticizing agent, thus increasing or decreasing T_g and a modulus of a nanocomposite. Depending on the number of organic groups (R) bearing reactive functionalities POSS can be classified as non-functional, monofunctional or polyfunctional.

Organic–inorganic hybrid materials were obtained by curing the epoxy resin (DGEBA) with an amine propyl isobutyl-POSS. This process was studied using DSC and TGA. The kinetic of polymerization reaction and the thermal degradation were analyzed based on an isoconversional model. The results showed that the activation energies of both processes (polymerization reaction and the thermal degradation) depend on the degree of conversion. Good thermal stability was observed for this system [196].

Monofunctional macromer 1-(3-glycidyl)propoxy-3,5,7,9,11,13,15-isobutylpentacyclo-[9.5.1.1(3,9).1(5,15).1(7,13)]octasiloxane (glycidylisobutyl-POSS) was reacted at 160 °C with low melting point aromatic diamines [4,4′-methylenebis(2,6-diethylaniline) (MDEA), 4,4′-diaminodiphenylmethane (DDM), and 4,4′-(1,3-phenylenediisopropylidene)bisaniline (BSA)], in a proportion rich in amine, to give precursors suitable for incorporation into an epoxy network. DSC demonstrated that an increase in the glass transition temperature took place without increasing the extent of cross-linking in the hybrid network. It was concluded, that such behavior arose from the nanoscopic size of the POSS cages, that hindered any motion of the molecular chains and network crosslinks [197].

Preliminary photoinduced cationic polymerization studies of novel epoxide silsesquioxanes were performed using catalytic triaryl sulfonium hexafluorophosphate (ASHP). Toluene solutions of POSS cubes (~20 wt.%) containing ASHP (0.5 mol.%) were coated on glass slides, dried and exposed to UV light (for 3–5 min, in air), providing insoluble, hybrid polymers. Polymerization was initiated by in situ formation of $H^+PF_6^-$ [198]. Epoxide substituted silsesquioxanes can be chemically, or photochemically cured to give hard, scratch- and solvent-resistant materials containing up to 65% masked silica [199].

Lee and Lichtenhan [67] investigated the thermal and viscoelastic properties of epoxy–POSS nanocomposites and found that the POSS could retard physical aging in the glassy state. Networks based on two different difunctional epoxies, DGEBA and 1,4-butanediol diglycidyl ether (BDGE) modified with 5 or 9 wt.% of cyclohexyl- and cyclopentyl substituted monoepoxy-functional POSS were cured with diamine-terminated poly(propylene oxide). A similar study investigated the thermal and viscoelastic property enhancement of crosslinked epoxies using two types of nano-reinforcement, namely, organoion exchange clay and polymerizable POSS macromer [199]. After chemical reaction with an amine hardener POSS cages remained as pendant groups in a polymer network. The introduction of these bulky structures led to a slight increase of T_g and retarded physical aging in the glassy state [68]. However, for an epoxy network reinforced with clay, any effect on the T_g observed was due to the presence of clay reinforcements [199].

Well-defined highly homogeneous silsesquioxane nanocomposites (NCs), with good-to-excellent control of the nanoarchitecture, were prepared from epoxy resins (DGEBA) and liquid octakis(glycidyldimethylsiloxy) octasilsesquioxane $[(glydicylMe_2SiOSiO_{1.5})_8]$ (OG–POSS) or solid octakis(ethyldimethylsiloxycyclohexenyl epoxide) (OC–POSS), by Laine et al. [105,200] (Fig. 21). They were cured within 10 h with diaminodiphenylmethane (DDM) at 150 °C under N_2 atmosphere. Only linear two-armed tethers were formed, in preference to 3- or 4-armed structures. Both nanocomposites had tensile properties comparable to common epoxy resin systems. The higher elastic modulus, observed for NCs based on OC, was explained by their poor nanoflexibility, that was stiffer than in the case of OG based NCs. A very low fracture toughness of OC/DDM was observed. The elastic moduli for the OG/DDM materials were typical of normal epoxy resins. Properties of NCs were dependent on NH_2/epoxy ratios [105,200].

Well-defined nanostructures were formed on curing (OG–POSS) and (OC–POSS) with diaminodiphenylmethane (DDM), wherein linear organic tethers of known structure joined only two cube vertices. TEM studies by Laine

and coworkers [201] revealed that these NCs were very homogeneous with no phase segregation, even at nm scale. TGA, DMA, room temperature mechanical properties, and molecular modeling suggested that nanocomposite thermomechanical properties may be modified by changing the tether architecture/rigidity. Surprisingly, OC/DDM elastic moduli increased from 2.2 to 3.3 GPa as the DDM content increased two-fold beyond the maximum crosslink density into a high defect density region, while the fracture toughness remained unchanged. Moreover, curing of OC–POSS and OG–POSS blends provided effective optimization of NCs properties, dominated by particular tethers.

Properties of silsesquioxane epoxy nanocomposite (OC/DDM) were also modified using core–shell rubber particles (CSR). The goal of that study was to form an epoxy resin system with enhanced thermal stability, elastic modulus, and fracture toughness. This resin had excellent elastic moduli and thermal stabilities at the expense of poor fracture toughness. A "single phase" hybrid OC/DDM nanocomposite (OC–POSS, 1.3 nm diameter) was used as a matrix for ∼100 nm diameter CSR reinforcing particles. Characterization of OC–POSS/DDM/CSR NCs showed that fracture toughness improved significantly on inclusion of CSR particles, with little effect on elastic moduli and thermal stability. Stress and strain at failure also improved, and fracture toughness doubled as a result of macroscale modification, while T_g, decomposition temperature, and elastic modulus remained nearly unaffected. SEM studies suggested that shear yielding and CSR pull-out were the likely sources of toughening [202].

A multifunctional POSS macromonomer, a polyhedral oligomeric silsesquioxane $[(PhCHCHO)_4(Si_8O_{12})(CH=CHPh)_4]$ (TES-POSS) (see Fig. 22), containing four epoxide groups and four styrene functionalities was blended and copolymerized with liquid aliphatic diepoxides, and cured with $H_2N(Et)CHCH_2CH_2NH_2$ as the hardener [203,204].

The epoxy–POSS composites (95/5 and 75/25 wt./wt.) were prepared by solution casting and then cured. Blends of epoxy resin with a ladderlike polyphenylsilsesquioxane (PPSQ) (Fig. 23) with a M_w of 4636 g/mol with compositions 95/5, 90/10, and 85/15 wt./wt. also were made and cured.
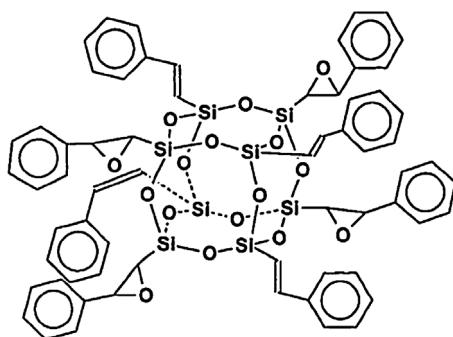
TEM observations revealed good dispersion of the POSS units in all the epoxide-POSS composites, presumably on the molecular scale, even at high POSS content (25 wt.%), in contrast to the aliphatic epoxy–PPSQ blends, that exhibited good miscibility and were transparent only at low PPSQ content (≤10 wt.%), while the (85:15) epoxy–PPSQ blend was opaque, that was probably caused by a partial phase separation. The crosslinked NCs based on aliphatic epoxy resins were characterized by increased and broadened T_g, increased the tensile and flexural modulus and improved hardness, but the flexural strengths of both epoxy–POSS composites and epoxy–PPSQ blends were lower than that of neat epoxy resin. These nanocomposites became harder and more brittle with increasing POSS content. The sharp decrease of the flexural strength of the epoxide-PPSQ blend reflected poor adhesion between the resin and PPSQ phase [203].

The low-viscosity aliphatic epoxides were also reacted with tetraepoxidized octa-2-styryl-POSS and aliphatic triamines and cured in five stages to 120 or 150 °C. The incorporation of 5 and 25 wt.% of TES-POSS into these epoxy resins gave an increase in the storage modulus in comparison with the neat epoxy. The increases in storage moduli were most pronounced above the T_g. The T_g increased as the maximum cure temperature was increased. DMTA measurements of tan δ vs. temperature gave a broadening and lowering of the intensity of the tan δ peak as the POSS content increased. No agglomeration of the POSS units was observed. This suggested that TES-POSS was molecularly distributed in the resin [204].

Epoxy based silsesquioxane materials were also studied by Mather and coworkers [205]. POSS-reinforced thermosets based on $[(glydicylMe_2SiOSiO_{1.5})_8]$ (OG) and 4,4′-diaminodiphenyl sulfone (DDS) as the curing agent were prepared. A thermal analysis showed that with an increasing amount of DDS, T_g of the cured OG system shifted to higher temperatures, and the storage modulus increased below and above T_g. TEM studies of the phase structure showed that as the amount of DDS in the OG system increased, the resulting phase structure became more homogeneous and continuous, but it had persistent 8–12 nm POSS-rich aggregates [205].

The addition of octafunctional cubic silsesquioxanes to epoxy resins led to improvement of the thermomechanical properties and the processability of aerospace-grade epoxy resin, especially by using a mixture of tetraepoxide (tetraglycidyl-4,4′-diaminodiphenyl methane) and

Fig. 22. Tetraepoxidized octa-2-styryloctasilsesquioxane (TES-POSS). Reprinted (adapted) with permissions from [203,204]. Copyrights: 2001, American Chemical Society, and 2001, Springer Science + Business Media B.V.
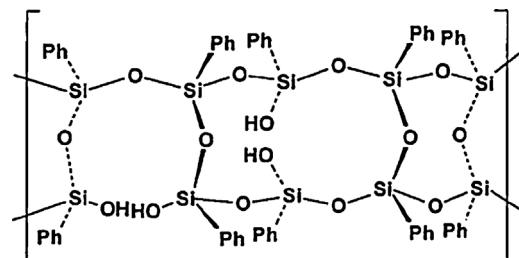
Fig. 23. The chemical structure of PPSQ copolymer. Reprinted (adapted) with permission from [203]. Copyright (2001) American Chemical Society.

Tetraglycidyl-1-2,4'-diaminodiphenyl methane

Butane diolglycidyl ether
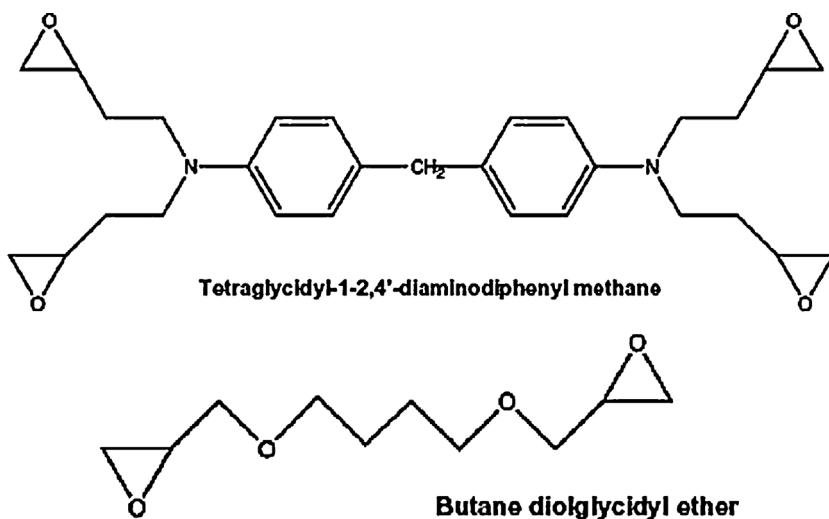
Fig. 24. Components of an aerospace grade epoxy resin. Reprinted (adapted) with permission from [206]. Copyright 2004 Wiley Periodicals, Inc.

diepoxide (butanediol glycidyl ether) (see Fig. 24). The storage modulus of the hybrids also increased, especially at the elevated temperatures, that is very important for aerospace applications [206].

Reactive, nanoporous particles of octakis(dimethyl-siloxypropylglycidyl ether)-silsesquioxane (OG) were introduced to epoxy resin to form low dielectric constant material for electronic industry. UV-cured epoxy resin and multiple reactive functional groups (oxirane ring) of OG reacted with photoinitiator to increase the curing density of the epoxy resin. The T_gs of epoxy increased with the increase of the OG content up to 10 phr due to the increase of the crosslinking density. Excessive aggregation at highest OG content of 15 phr resulted in the reduced crosslinking density and T_g. The char yield of the composite increased with the increase of OG content because stable products (Si and SiO_2) were formed after thermal decomposition. The presence of OG led to the higher porosity and thus to the lower dielectric constant [207].

The commercial epoxy resin (DGEBA) was also modified with 1-(3-glycidyl)-propoxy-3,5,7,9,11,13,15-isobutylpentacyclo[9.5.1.1(3,9).1(5,15).1(7,13)]octasilses-quioxane (glycidylisobutyl-POSS) (Fig. 25). Next it was cured with 4,4'-diaminedimethylmethane (DDM), at 160 °C [208].

$R = i\text{-butyl}$
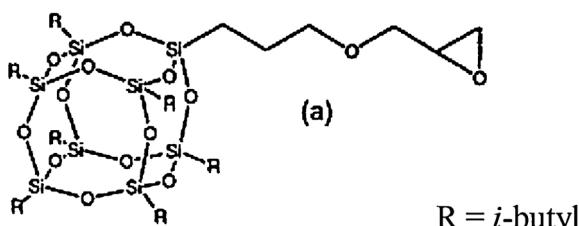
Fig. 25. The molecular structure of the glycidylisobutyl-POSS. Reprinted (adapted) with permission from [208]. Copyright 2005, Elsevier.

First, the POSS and DDM, in a proportion 1:4, were dissolved in tetrahydrofuran at room temperature, then the solvent was evaporated at 60 °C for 24 h. The resulting solid was milled, heated to 160 °C, and kept at this temperature for 120 min, to complete the epoxy amine reaction. The polymer network was synthesized adding stoichiometric amount of DGEBA, mixing at about 115 °C, pouring the solution into a glass and curing at 160 °C for 40 min. The resulting polymer network contained 64% of (glycidyl)isobutyl-POSS fraction [208]. The nanocomposites of octa(aminophenyl)silsesquioxane (OAPS) (Fig. 26) with diepoxides or dianhydrides provided high cross-link density materials with good thermal stability, and good-to-excellent tensile and compressive strengths [105,209].

Selected epoxy-functionalized cube NCs with tethered architectures (see Scheme 37) were prepared from octa(aminophenyl)silsesquioxane $[NH_2C_6H_4SiO_{1.5}]_8$ (OAPS), poly(aminophenyl)silsesquioxane (PAPS) (Fig. 26), octa(glycidyldimethylsiloxy)octasilsesquioxane $[(glycidyl-Me_2SiOSiO_{1.5})_8]$ (OG), DGEBA and diaminodiphenylmethane (DDM) [210]. It was found that:

(1) tethers with aromatic components increased char yields and decomposition temperatures,
(2) cube loadings were important in thermal stabilities,
(3) aromatic tether structure, short lengths and high cross-link densities reduced tether segmental relaxation motions that minimize macroscopic glass transitions.

Nanocomposites prepared from OAPS and PAPS (Fig. 26) exhibited nearly identical thermo-mechanical properties, while PAPS is the less expensive substrate than OAPS. NCs with high silica contents and short tethers were quite thermally stable but quite brittle. It was also demonstrated that the architecture of the organic tethers between vertices can be changed to optimize rigidity, processability and resulting thermomechanical properties [211]. Although bulk ceramic materials are very brittle, very thin ceramic fibers
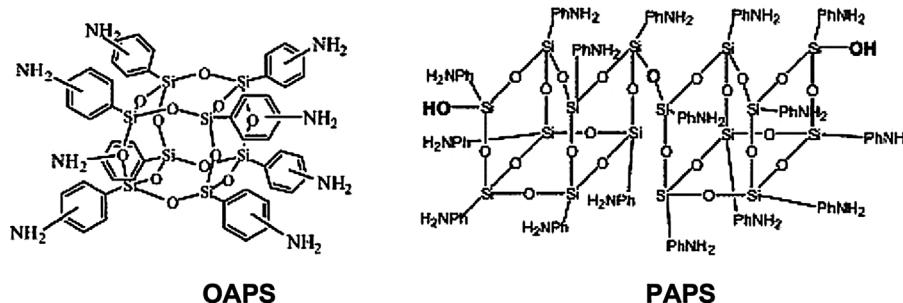
Fig. 26. The molecular structures of OAPS and PAPS. Reprinted (adapted) with permission from [210]. Copyright (2004) American Chemical Society.
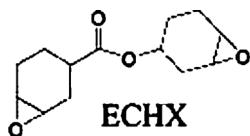
Fig. 27. The chemical structure of diepoxide ester ECHX.

and films of these materials exhibited excellent mechanical properties because the energy required to initiate cracks leading to catastrophic failure is often beyond normal use conditions. It was suggested that thin films and fibers of the produced materials may also exhibit excellent mechanical properties that rival some ceramics [211].

Single-phase materials were developed that offer control of the coefficients of thermal expansion (CTE) of silsesquioxane–epoxy systems over an order of magnitude. Such resin thermosets were prepared from a series of epoxides: OC–POSS and OG–POSS, DGEBA, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECHX) (Fig. 27), or tetraglycidyl-m-xylenediamine (TGMX), and cured using $[NH_2C_6H_4SiO_{1.5}]_8$ (OAPS). The ratio of NH_2:epoxy groups was either 0.5 or 1.0 [212]. The examined epoxy systems exhibited cure behavior typical of commercial epoxy resins, and CTEs as low as 22 ppm/°C. However commercial, low viscosity epoxy resins, especially those made with DGEBA, usually exhibit

CTEs in the 60–200 ppm/°C range. Control of CTE is of considerable importance in multiple materials applications (e.g., coatings that offer resistance to abrasion, corrosion, photooxidation, hydrophobicity, staining, etc.), for which the polymer coatings are applied to glass, ceramic, or metal substrates with quite dissimilar CTEs. In such cases, thermal cycling often leads to loss of adhesion followed by coating failure via chemical and/or mechanical mechanisms [212].

Nanocomposite films with exceptional oxygen barrier properties, competitive with current commercial grade barrier films, were prepared by the reaction of octaaminophenyl–silsesquioxane (OAPS) with a variety of epoxides and dianhydrides and their subsequent heat treatment [213]. While cast OAPS/ODPA and OAPS/ECHX epoxide films had promising oxygen transmission rates (OTRs) of 25 and 6 cm³ 20 μm/(m² day atm) (at optimum curing conditions), and significant improvement was achieved with warm pressing. A combination warmpressed, bilayer film system consisting of OAPS/ECHX and OAPS/TGMX was found to have the lowest OTR, <1 cm³ 20 μm/(m² day atm). Commercial barrier films with similar performance are usually achieved with three or four different film layers and may utilize adhesives to keep the films together. The silsesquioxanes films can be further functionalized to tailor barrier properties or for selected transport of specific gases for separation applications, particularly

(a) tether formation from epoxy cubes and DDM

(b) tether formation from OAPS and the commercial epoxy resin (DGEBA)
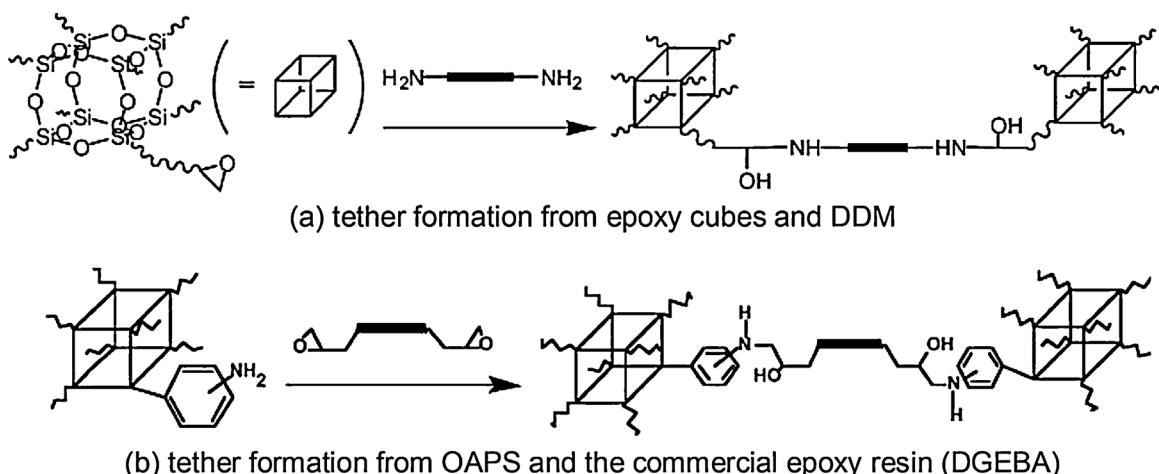
Scheme 37. The preparation of tethered POSS nanocomposites. Reprinted (adapted) with permission from [210]. Copyright (2004) American Chemical Society.

OAPS/imide and OAPS/epoxide films, provided excellent O_2 barrier properties, potentially of use for a wide variety of packaging applications. These silsesquioxane films were thermally robust, especially the OAPS/imide films (>500 °C when fully cured). The silsesquioxane NCs offer higher barriers to N_2 diffusion than O_2 and high thermal stability of potential use in high-temperature electronics packaging and encapsulation applications. These results contrast considerably with polysiloxane films, well-known to have high oxygen permeabilities [>19 000 cm³ 20 μm/(m² day atm)] due to the high degree of chain flexibility [213].

Abad et al. [121] utilized a POSS containing one epoxy group and seven isobutyl groups per molecule. They incorporated this cubic filler into an epoxy resin based on DGEBA and 4,4′-[1,3-phenylenebis(1-methylethylidene)]bis(aniline) as a hardener. They observed a macrophase separation into epoxy-rich and POSS-rich regions, possibly derived from the incompatibility of the isobutyl groups attached to the POSS with the aromatic epoxy–amine network. A secondary phase separation occurred in the epoxy-rich phase, during polymerization, producing a dispersion of small POSS domains. It was noticed that most POSS-rich domains were amorphous, and only a small fraction of POSS crystals was detected. The higher T_g observed for the POSS-modified epoxy may be associated with the hindering of polymer chain motions by their covalent bonding to POSS clusters.

Chiu et al. [122] used (isocyanatopropyl)dimethylsilyl (isobutyl) POSS in a reaction with DGEBA to synthesize the side-chain polyhedral oligomeric silsesquioxane-type epoxy hybrid material (IPEP). The particle sizes of the POSS segment were less than 5 nm and they were dispersed uniformly. The IPEP-DGEBA hybrid material had amorphous structure. The POSS segment in IPEP improved the thermal degradation activation energies, the char yield, and also the antioxidation properties in the air atmosphere. Improved hardness of these materials%, was also observed for IPEP contents of the IPEP-DGEBA composites less than 50 wt.%.

Octafunctional POSS can form highly cross-linked networks through their eight functional groups and exhibited unique thermal and mechanical characteristics. Xiao et al. [107] cured two octakis substituted POSS, bearing eight epoxy groups per molecule [octakis-(dimethylsiloxypropylglycidyl ether)silsesquioxane and octakis(dimethylsiloxyethylcyclo-hexenylepoxide)silsesquioxane] with 4,4′-methylenebis(cyclohexylamine) and 4-methylhexa-hydrophthalic anhydride, as hardeners. Due to the multifunctional structure of the POSS hybrid materials the DGEBA-POSS hybrid composites were highly crosslinked networks and the polymer main framework could not move freely. The thermochemical data from DSC analysis and FTIR showed that the curing reactions of the POSS modified epoxy resin were more difficult than neat DGEBA resin, because of a steric hindrance. The unique thermal and mechanical properties of these POSS composites could be useful for high temperature applications [107].

Win et al. [214] prepared crosslinked neat epoxy resin DGEBA and nanocomposites composed of 5 or 10 wt.% of a commercial viscous liquid mixture of polyepoxy–POSS, with a general formula $(RSiO_{1.5})_n$ [$n = 8$,

10, 12; R = $(CH_2)_3OCH(O)CH_2$]; both were cured with the tetrafunctional aromatic diamine: trimethylene glycol di-p-aminobenzoate. It was found that just below T_g the thermal pressure coefficient γ was ~20% smaller for the polymer nanocomposite containing 10 wt.% POSS, than for the neat epoxy resin.

Liu and co-workers [215] obtained epoxy–POSS nanocomposites (NCs) from octakis(glycidyloxydimethyl-siloxy) POSS and DGEBA cured with low molecular weight curing agents of diethylphosphite (DEP) and dicyanodiamide (DICY). Both hardeners reduced the steric hindrance in curing reaction, increased the reaction conversions and improved the homogeneity of the resulting nanocomposites. Materials with high POSS contents of 35–54 wt.% exhibited good thermal stability, improved flammability, and high storage moduli. The improved flame-retardancy of the NCs was demonstrated by increases in the LOI values up to 41%.

Mya et al. [123] used UV radiation in the presence of a cationic photoinitiator to polymerize mixtures of multifunctional epoxy monomers: GPTMS, product of partial hydrolysis and condensation of GPTMS, trimethylopropane triglycidyl ether (TMPTGE), octaepoxy-functionalized POSS, and methyl silicate and obtained products. These were of interest as they may be particularly useful in preparing lenses having light weight and high refractive index; polythiourethane (PTU) with refractive index of 1.60–1.67 was used as a polymer substrate for this purpose. At the initial state the surface of hybrid coatings was smooth and had excellent adhesion to the substrate, but after the exposure to the sunshine the surface became rough, and adhesion failure occurred by photodegradation on the PTU substrate during weathering. The addition of UV absorbers significantly protected the polymer substrate from the photodegradation.

A novel POSS containing eight 3-mercaptopropyl groups (MPOSS), synthesized by Fu et al. [72], was used to modify an epoxy–amine network, cured by aliphatic anhydride, followed by a co-curing reaction with DGEBA. The miscibility between epoxy and MPOSS occurred at a relatively high filler content and the MPOSS reinforcing effect on the epoxy was observed as well as the transition of the brittle stage of neat epoxy resin to a ductile stage of the nanocomposite and correlated well with the large increase in the impact strength. MPOSS–DGEBA epoxy hybrids exhibited lower thermostability at a lower temperature but higher thermostability and higher efficiency in char formation at the elevated temperature. The MPOSS–epoxy hybrids had a lower T_g than that of neat epoxy system.

Amino-functionalized POSS [$(NH_2(CH_2)_3)_8Si_8O_{12}$] has often been used for the preparation of epoxy nanocomposites. Zhang et al. [216] first reported the incorporation of octa(aminopropyl) POSS–NH_2 into thermosetting epoxy resin DGEBA, cured by DDS. When the POSS content was high enough to form a silica-layer on the surface of materials during the decomposition studies, T_{dec} was increased with POSS loading, and the average activation energy of thermal decomposition was raised from 102 to 113 kJ/mol, associate with changes of the thermodegradation mechanism of tested composites. Every DGEBA–POSS–NH_2 hybrid system was a homogeneous composite, with a

storage modulus higher than that of the neat epoxy resin in the glassy state. The T_g as well as the char residue increased monotonously with the increase of POSS–NH$_2$ content.

Gao and co-workers [217] investigated the o-cresol formaldehyde epoxy resin (o-CFER) with polyhedral oligomeric silsesquioxane containing eight N-aminoethyl-3-aminopropyl groups (AEAP-POSS). The materials exhibited increasing T_g with increase in the AEAP-POSS content, to maximum 107 °C for a molar ratio of amino groups to epoxy groups of 0.5. The nanocomposites with a higher percentage of AEAP-POSS exhibited enhanced thermostability. The effect of AEAP-POSS on the increase of mechanical properties (the tensile and the impact strengths) and electric properties (dielectric constant ε, dielectric loss factor tan δ, volume and surface resistivity) was also observed.

The epoxy resins have been applied in electrical insulation systems for a long time. Nanocomposites based on epoxy networks filled with nanoparticles of layered silicates, silica, TiO$_2$, Al$_2$O$_3$ or ZnO are used as epoxy nanodielectrics. These organic–inorganic NCs show good electrical insulation, higher breakdown voltage and resistance to partial discharges, as compared to neat epoxy resins reinforced with microsized fillers. Very good epoxy insulating systems have been obtained by the use of POSS nanofillers. Chen et al. [218] prepared good nanodielectric materials using octa(dimethylsilylylglycidyloxypropyl) POSS (OGDMS), cured with aromatic diamine. This highly crosslinked system was characterized by a distinct increase in glass transition temperature by 80 °C, in comparison to the T_g of the reference epoxy network of DGEBA and aromatic diamine.

Takala et al. [219] synthesized epoxy–POSS nanocomposites useful in a high voltage applications. These hybrid polymers were prepared with DGEBA epoxy resin, containing up to 10 wt.% of glycidyl–POSS and octa(glycidyloxypropyl)–POSS units, cured with anhydride hardener. The incorporation of the POSS molecules into epoxy networks gave materials with decreased T_g with increasing POSS content – in comparison with T_g of neat epoxy resin – due to a soft interphase formed by the flexible subsituents of the nanoparticles.

Matejka et al. [66] investigated the rubbery epoxy–POSS nanocomposites, that were prepared from DGEBA epoxy resin, poly(oxypropylene)diamine (POPDA), mono-epoxy POSS and multi-epoxy POSS cages. The NCs obtained contained POSS attached as pendant units on the polymer chains or as cubic segments of organic–inorganic network. Incorporation of octa(hexylepoxy)-POSS into the epoxy network led to the increase in rubbery modulus due to enhaced crosslinking density. However, T_g decreased as a result of the soft shell of POSS flexible organic substituents forming a soft organic–inorganic interphase. Improved thermal stability was observed for epoxy networks containing POSS units bearing phenyl group, whereas POSS flexible junctions affected a first thermal degradation step.

Matějka and coworkers [125] also prepared two types of epoxy–POSS nanocomposites of DGEBA-aliphatic diamine and a mono-(POSS-E1) and an octaepoxy functionalized POSS (POSS-E8). Homogeneous dispersion of POSS fillers in DGEBA networks were observed in the case of POSS-E8 nanocomposites, whereas the pendant POSS-E1 were

aggregated and formed large crystalline domains. The properties of the two types of hybrid materials were quite different. NCs with pendant POSS-E1 showed low T_g, low thermal stability and the high dielectric loss factor at higher temperatures, while NCs with high crosslinking density (POSS-E8) exhibited the high resistivity (10^{15} Ω m) and the low dielectric loss factor, especially at temperature above 50 °C, and showed improved thermooxidative stability and enhanced thermomechanical properties with increasing POSS content.

Three kinds of ladderlike polyepoxysiloxanes were self-cured at 200 °C for 2 h [108] or with 1,3-bis(aminopropyl) tetramethyldisiloxane at 40 °C and 200 °C [109]. These reactions were investigated by contact angle measurements and surface free energy study. Several factors (such as diamine amount, reaction time, and temperature) affected the system surface tension or a surface free energy. The experimental results showed that an increase in the diamine amount in the reaction systems resulted in the increase in the polar part of a surface free energy. However, because epoxy (electron acceptor) and diamine (electron donor) react fast at elevated temperatures, increasing reaction temperature caused decrease the polar part of the surface free energy, while increased the nonpolar part of the surface free energy. The evolution of the surface free energy with time for various epoxy–diamine reaction systems at various temperatures were also studied. It was found that it took a relatively long time (50–60 h) to reach the equilibrium state.

Zheng and coworkers [114] reported the synthesis of organic–inorganic poly(hydroxyether of bisphenol A) (PHE-BA) copolymers with POSS in the main chains through the direct polymerization between diepoxy and bisphenol A.

An organic–inorganic hybrid NCs were prepared by Ramirez et al. [220] through reaction of (octaepoxy)silsesquioxane (OE-POSS), with an epoxy–amine system (Fig. 28).

OE-POSS (2.5, 5, 7.5, 10, 20, 30, or 50 wt.%) partially replaced the thermosetting resin (DGEBA), in its reaction with an aromatic diamine, 4,4′-(1,3-phenylenediisopropylidene) bisaniline (BSA). The presence of POSS accelerated the rate of opening of glycidyl epoxy rings of DGEBA. The values of the T_g seemed to increase with the increasing cure temperature, because of the higher cross-linking degree obtained, but decreased with the content of OE-POSS, due to the hindrance that POSS molecules caused in the system [220].

When DGEBA and 3,13-diglycidyloxypropyloctaphenyl double-decker silsesquioxane (diglycidyloxypropyl DDSQ) were used as the diepoxy monomers (Scheme 38), it was found that with the direct polymerization PHE-BA copolymers with POSS in the main chains of polymers can be successfully obtained, while the content of diglycidyloxypropyl DDSQ was not very high [114]. The T_gs of the organic–inorganic PHE-BA copolymers depended on the contents of POSS in the copolymers. TGA indicated that the stability of the copolymers was significantly improved in terms of the temperatures at the maximum rate of degradation and the yields of degradation residues. Owing to the presence of POSS in the main chains, the surface
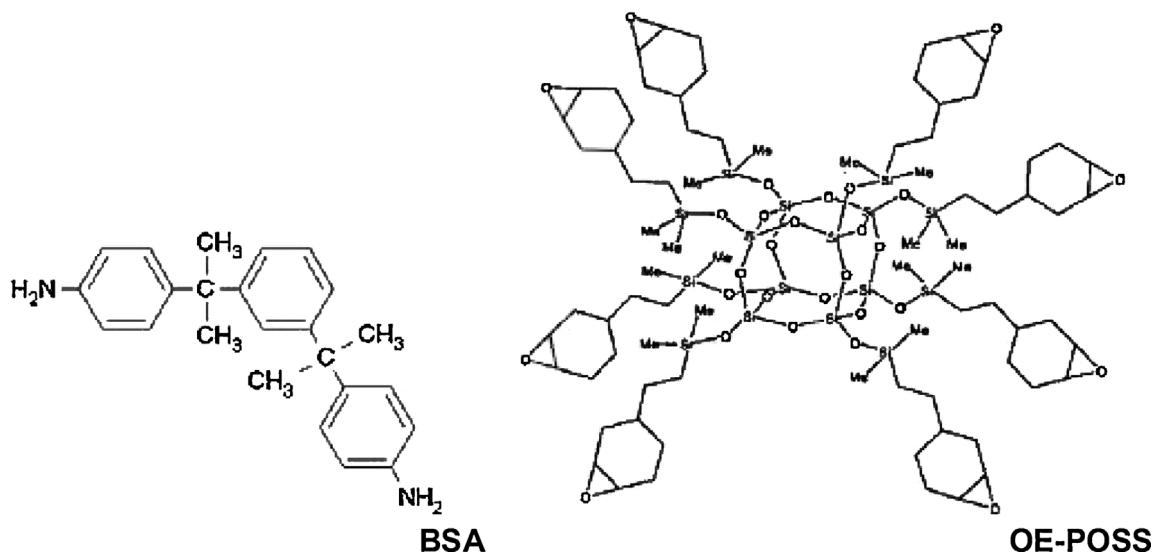
Fig. 28. The molecular structures of BSA and octaepoxy–POSS. Reprinted (adapted) with permission from [220]. Copyright 2008, Elsevier.
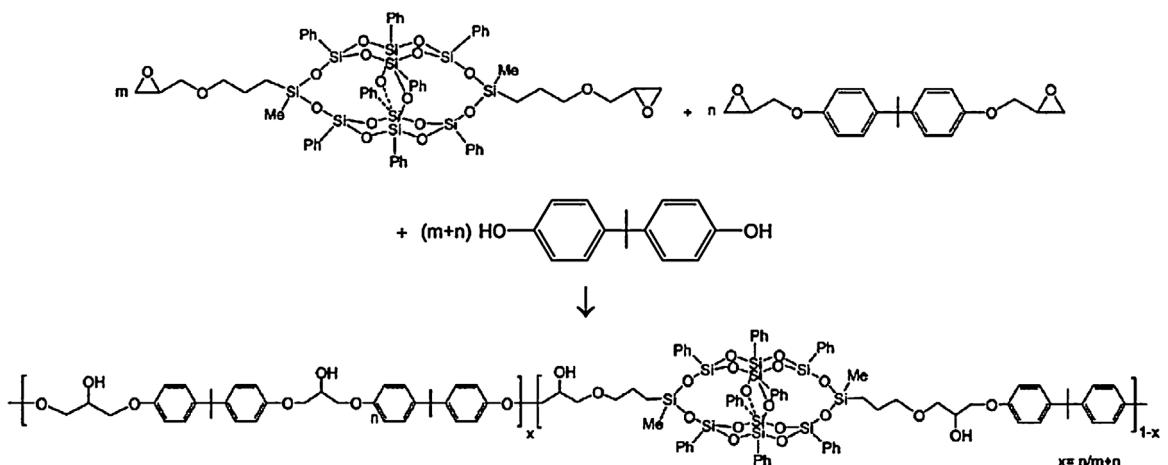
Scheme 38. The synthesis of organic–inorganic poly(hydroxyether of bisphenol A) copolymers with POSS in the main chains. Reprinted (adapted) with permission from [114]. Copyright© 2011, Royal Chemical Society.

hydrophobicity of the organic–inorganic copolymers was significantly improved compared to unmodified PHE-BA [114].

The thermal degradation behavior of poly(methyl-phenyl)silsesquioxane–epoxy resin (PMPSQ–EP) systems were investigated by thermogravimetric analysis (TGA) under non-isothermal conditions in nitrogen atmosphere [221]. The results showed that a remarkable increase of activation energy was observed in the presence of PMPSQ (Scheme 39), that indicated that the addition of PMPSQ retarded the thermal degradation of EP. PMPSQ significantly increased the activation energy of EP thermal degradation especially in the early and final stage of thermal degradation process, indicating that the PMPSQ stabilized the char layer and improved the flame retardancy of EP in the early and final periods of the thermal degradation process.

The rubbery epoxy network, based on DGEBA and poly(oxypropylene)diamine, was reinforced with a nanometer-sized inorganic building blocks—POSS. The organic–inorganic networks contained POSS as pendant units of a network chain or as network cross-links of different functionality. Thermomechanical properties and thermal stability of the POSS-containing networks
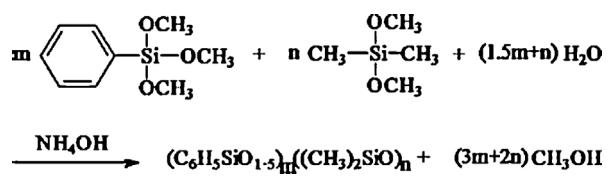
Scheme 39. The synthesis of PMPSQ. Reprinted (adapted) with permission from [221]. Copyright© 2011 Wiley Periodicals, Inc.

were determined by DMA and TGA. The strongest reinforcement was achieved in the networks with pendant POSS forming ordered crystalline domains, that acted as physical crosslinks. The POSS skeleton with "soft" flexible substituents, e.g., octyl, showed formation of weak aggregates that did not contribute to reinforcement. The rubbery modulus of the networks with POSS in a junction grown with increasing POSS functionality, due to enhanced network cross-link density. These networks were more homogeneous, and the modulus of the network with the octafunctional POSS junction well agreed with theoretical prediction. The mechanical properties were affected mainly by POSS–POSS interactions, while the POSS-network chain interactions were of minor importance [65].

4.4. Flammability of neat and modified epoxy resins

The epoxy resins used in electronics should be stable at temperatures higher than 300 °C. In order to extend their applications as electronic materials, and in the aerospace industry, it is crucial to improve their thermal and flame resistance. Halogenated compounds were widely used as fire retardants in the past. Bromine and antinomy flame retardants release highly toxic, corrosive and carcinogenic products during their combustion, therefore they are not used recently.

A traditional technique in the preparation of flame retardant epoxy resins is to blend the flame retardant additive with the polymer. This method has some shortcomings, such as low efficiency of the flame retardant, leaking out during processing and usage, and detrimental effects on the thermal and mechanical properties of the polymer, because there is no chemical bonding between the flame retardant additive and the polymer. In contrast to additive-type flame retardants, for thermosetting resins, it is more common to use reactive flame retardants, that can form chemical bonding to the polymer chains. For epoxy resins most of the reactive flame retardants contains oxirane and/or amine groups. Phosphorus-containing compounds with their low generation of smoke and toxic gases, and the high flame retardant efficiency are very attractive flame retardants [222]. Phosphorus-containing polymers confer fire resistance mainly by modifying the thermal decomposition of the polymers, forming a surface layer of a protective char during a fire until the unburned material begins to decompose. The formation of a stable char is one of the desirable mechanisms of flame retardation in polymers because the char layer acts both as a thermal insulator and as a barrier to oxygen diffusion. The char acts as the barrier to inhibit gaseous products from diffusing to the pyrolysis zone and to shield the polymer surface from heat and air. Silicon-containing polymers can degrade, forming thermally stable silica, that has the tendency to migrate to the char surface as the protection layer to prevent further degradation of the char at high temperature.

The enhancement of flame retardancy of epoxy resins was achieved by incorporation of phosphorus and silicon into epoxides. On exposure to a flame, phosphorus provides a tendency for char formation, silicon provides the enhancement of thermal stability of the char and often a synergistic effect of P–Si flame retardation was observed. Hsiue et al. [223] achieved improvement of the flame retardancy of the epoxy resin through the introduction of an organic–inorganic hybrid nanostructure into epoxy polymeric system. They obtained epoxy nanocomposite from DGEBA, bis(3-glycidyloxy)phenylphosphine oxide, diaminodiphenyl methane and TEOS, in the presence of (p-toluenesulfonic acid) as the catalyst, via in-situ sol–gel process. The T_g of the hybrid epoxy resins increased with the silica content and the nanosized silica showed improvement of the flame retardant properties of epoxy resins. The phosphorus-silica synergistic effect on the limiting oxygen index (LOI) enhancement was also observed with a high value of 44.5.

Phosphorus-containing epoxy-based epoxy–silica nanohybrid materials were obtained by Liu et al. [126] from bis(3-glycidyloxy)phenylphosphine oxide, diaminodiphenylmethane, and TEOS in the presence of p-toluenesulfonic acid via an in situ sol–gel process. A mixture of two phosphorus conaining alkoxysilane isomers was prepared by the reaction of a cyclic phosphorus compound 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and (3-glycidoxypropyl) trimethoxysilane (GPTMS). These new fire retardant compounds were added to the conventional epoxy (DGEBA) curing composition. A sol–gel reaction of GPTMS was performed simultaneously with epoxy curing reactions, so that the epoxy resin-silica network was formed. The silica formed on a nanometer scale in the epoxy resin was characterized with FTIR, NMR, and SEM. The resulting hybrid epoxy resins exhibited the high T_g (167 °C), good thermal stability over 320 °C, and increased LOI of 28.5. The glass-transition temperatures of the hybrid epoxy resins increased with the silica content. The in situ formed nanosilica showed an enhancement effect of improving the flame-retardant properties of epoxy resins. The synergism of P–Si on flame retardance was also observed, since both these atoms are able to form ceramic residues.

Spontan et al. [127] prepared phosphorus- and silicon-containing epoxy resins from diglycidyl ether of (2,5-dihydroxyphenyl)diphenyl phosphine oxide (Gly-HPO), diglycidyloxymethylphenylsilane (DGMPS) and 1,4-bis(glycidyloxymethylsilyl)benzene (BGDMSB) as epoxy monomers, and DDM, bis(4-aminophenoxy) dimethylsilane (APDS) and bis(3-aminophenyl)methyl phosphine oxide (BAMPO) as curing agents. They found that the most reactive monomer was DGMPS and the most reactive curing agent was APDS. The high LOI values (37–38) for epoxy resins containing heteroatoms in contrast with LOI ≈24 for the neat epoxy resins (prepared from DGEBA and cured with DDM), confirmed that epoxy materials having P and Si atoms were effective flame retardants, but any synergistic effect of phosphorus and silicon on flame retardation was not observed. It was noticed that the presence of phosphorus in phosphorus-containing epoxy resins increased the LOI values, even when the phosphorus content was low, but for the silicon-containing epoxy resins the LOI values increased with increasing silicon content up to 10%.

DOPO is a cyclic phosphate with high thermal stability, good oxidation and water resistance. DOPO or

its derivatives have been quite often used as effective flame retardants for epoxy resins [224–226]. Zhang et al. [227,228] successfully synthesized DOPO-POSS molecules with high thermal stability and used them as the flame retardant in epoxy DGEBA resins. A nanoscale dispersion of DOPO-POSS in the composites was obtained, and an interesting phenomenon, named the "blowing-out extinguishing effect through a pyrolytic gas spurt" was observed during the UL 94 test for DGEBA with 2.5 wt.% DOPO–POSS loading with the LOI value 30.2. It was observed that the increase of DOPO–POSS content had a positive effect on the thermal stability and char yield of DOPO–POSS–DGEBA composites. However, the flame retardancy of epoxy resins decreased as the DOPO–POSS content increased from 3.5 wt.% to 10 wt.%.

The use of phosphorus compounds and POSS molecules to improve thermal properties, oxidation resistance and flame retardancy of almost all kinds of thermoplastic or thermosetting polymers has been reported in recent years. Chiu et al. [229] prepared a series of thermally stable hybrid NCs from two epoxy systems: DGEBA and DGEBA modified with (3-isocyanatopropyl)triethoxysilane (DGEBA–IPTS), filled with POSS containing phosphorus atoms, formed in sol–gel process from [2-(diphenylphosphino)ethyl]-triethoxysilane, cured with TEOS and aromatic diamine. These NCs exhibited good miscibility between organic and inorganic phases with well dispersed POSS particles. In DGEBA-POSS system the activation energies of thermal degradation, calculated by the Kissinger and Ozawa methods were 150–209 kJ/mol and 159–209 kJ/mol, respectively, and they were significantly lower in comparison with DGEBA–IPTS–POSS system: in the range 170–305 kJ/mol and 180–402 kJ/mol. The activation energies of thermal degradation increased with POSS content, however higher POSS content interfered the epoxy–amine curing reaction and decreased the thermal stability, so the optimum content of POSS in these materials was 9 wt.%. The obtained NCs showed LOI value above 30, and their excellent thermal stability and flammability could be attributed to the P and Si synergistic effect of POSS containing phosphorus atoms.

Self-contained silicon compounds can also be used as flame-retardants, due to their very high termal stability. The presence of silicon-containing polymers led to the formation of continuous silica layers that retarded oxidation of char and increased LOI values. Such protective layers were especially effective in oxygen containing materials (polyesters, polyurethanes, epoxides or cellulose) [230–232]. However, it is commonly known that silicones and epoxy resins are incompatible, and that always caused some difficulties during their blending. Hsiue et al. [124] synthesized a polymer containing both siloxane and epoxy linkages, by curing dicyclopentadiene-containing glycidoxy group with various disiloxanes terminated with amino groups, as the curing agents. The silicon-containing epoxide compositions showed higher thermal resistance and higher char yields than the silicone-free resin. The relatively high LOI values of 31 to 34 for these hybrid materials confirmed the effectiveness of the epoxides modified with silicon-containing fire retardant additives.

Polyhedral oligomeric silsesquioxanes have often been used to reduce a tendency of a conventional epoxy–amine system to undergo combustion. Ramirez and coworkers [233] tested novel inorganic–organic hybrid materials, obtained from DGEBA epoxy resin and octaepoxy–cyclohexyldimethylsilyl-POSS (OE-CH-POSS), that were cured with derivatives of bisaniline (BSA). It was observed that the POSS–DGEBA–BSA composites increased the resistance to degradation of the blend with the percentage of POSS in inert and oxidation atmospheres. The char yield values increased with the content of OE–CH–POSS and a better flame retardancy was exhibited in the samples with the higher content of OE–CH–POSS. Wu et al. [234] synthesized a partial T_8 cage structure containing diglycidyl isocyanurate functionality and used it to prepare DGEBA composites in order to improve their flame retardancy, and thermal and oxidation resistance. It was found that the presence of T_8 changed the mechanism of thermal degradation of the epoxy resin, retarding the movement and scission of the main chain of DGEBA. It was also assumed that cage structure T_8 could capture the hydrogen and hydroxyl radical and form a stable charred layer in the condensed phase that would prevent the underlying materials from further destruction during combustion.

Su et al. [235] investigated organic–inorganic hybrids comprising the epoxy resin and POSS containing silanol groups, prepared via in-situ polymerization of DGEBA and DDM. These composites with a single T_g were homogeneous, transparent materials, in which organic and inorganic moieties were joined by covalent bonds. The thermal stability of the hybrids was higher than that of neat epoxy resin considering the char yields of the hybrids and pure polymer, and the char yield of the composites increased with the inorganic content. The authors suggested that the POSS content could prevent thermal degradation of the polymer matrix and retain significant amounts of the char in order to stop the spreading of fires. The so called "*integral procedural decomposition temperature*" (IPDT) was correlated with the volatile compounds of polymeric materials, and was used to estimate their inherent thermal stabilities. The IPDT of pure DGEBA was found to be 702 °C, the values for hybrids with 10, 20, 30, 40 wt.% of POSS were 802 °C, 1009 °C, 1306 °C and 1559 °C, respectively. High-temperature thermal stability was increased by addition of POSS, because the final product of the thermal decomposition was silica, that could not degrade further. Thus, inorganic components could improve the thermal stability of the epoxy resin as well as retard the oxidation of DGEBA and enhance its thermal oxidation resistance.

Recently it was reported that expandable graphite (EG) can improve the flame-retardance of polymer coatings. Since the compatibility between polymer matrix and EG is poor, so it was necessary to functionalize EG by silane coupling agents to increase the interaction force between organic and inorganic phases. Chiang and Hsu [236] modified DGEBA resin and EG with (3-isocyanatopropyl)triethoxysilane (IPTS). They obtained a novel epoxy–EG composite from these components and DDM via sol–gel method. The silane functional groups attached on the surface of EG led to the covalent

bonding between organic and inorganic phases, enhancing the compatibility between the filler and polymer and effectively improved the thermal stability of composites. The IPDT value of pure DGEBA was 640 °C, and for composites with 10, 20, 30 wt.% of EG increased to 767 °C, 1031 °C and 1289 °C, respectively. It was also observed that the inorganic component could suppress the formation of toxic gases liberated from the composite during its combustion process. Such composite materials are safer for people and help them to survive the fire conditions.

4.5. Composites of epoxides modified with polyurethanes and silanes

The epoxy resins are a important class of highly crosslinked thermosetting polymers that show brittle properties, poor impact resistance and a low fracture toughness. The epoxy resins modified with reactive liquid elastomers, e.g., carboxyl-terminated poly(butadiene-co-acrylonitrile) rubbers (CTBN) or crosslinked elastomers, dispersed in epoxy resins, showed the improved fracture toughness [128,237–241].

A new type of block poly(urethane-co-imide) elastomers that exhibited better thermal and mechanical properties than traditional liquid elastomers was prepared recently [242]. Alternatively, the mechanical properties, chemical and thermal stability of epoxy resins was improved by dispersing ceramic particles (e.g., silica) into epoxy networks. The sol–gel process is one of the best way to obtain high performance polymer–SiO$_2$ hybrids at low temperature. Compared with blending method, in situ process through sol–gel reaction causes much stronger interactions between organic and inorganic phases. In the sol–gel method, the alkoxysilane, e.g., TEOS, CFS and alkoxysilane-functionalized elastomers are often used as precursors of silica in order to modify properties of the epoxy resin. J. Song et al. [242] also described the synthesis of novel triethoxysilane-functionalized poly(urethane-imide) (PUI–Si) (Scheme 40), that was introduced into the epoxy matrix to prepare EP–PUI–Si nanocomposites by the in situ sol–gel process and crosslinking reactions.

The addition of 50 wt.% of PUI–Si to the epoxide improved the thermal properties of NCs by the increase over 150 °C of the initial decomposition temperature, in comparison with the neat epoxy resin. Nanocomposite containing 70 wt.% of PUI–Si showed a hydrophobic surface characterized by the water contact angle that increased to 97.4°. In EP–PUI–Si composites the silica nanoparticles were smaller than 20 nm and strongly interacted with the epoxide matrix. Improvement of the tensile strength and elongation at break of the above NCs was also observed.

Liu et al. [243] reported that polyurethane (PU) composites containing imide structure and epoxy resins showed higher thermal stability and much better chemical resistance, due to the presence of the thermally stable imide structure and the interaction between PU and epoxy resins through chemical bonds. Based on these data, in another work they tried to incorporate imide structure, silica and epoxy into PUs for improving thermal stability, and extending the properties of the new PU–epoxy–silica composite [244]. The poly(urethane-imide) PUI was synthesized in
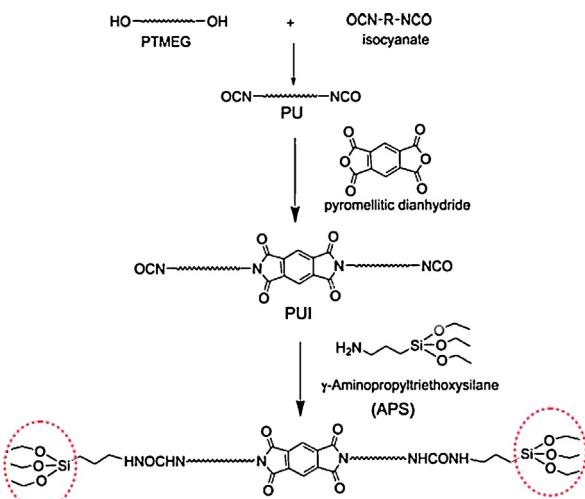
Scheme 40. The synthesis of alkoxysilane-substituted PUI–Si. Reprinted (adapted) with permission from [242]. Copyright© 2011 Society of Chemical Industry.

the reaction of trimellitic anhydride with isocyanate-terminated PU prepolymer. The as-synthesized PUI was then directly polycondensed with silane-modified epoxy resin DGEBA via a polyfunctional aziridine crosslinker and sol–gel process to obtain new PUI–epoxy–SiO$_2$ hybrids. The thermal stability and mechanical properties of PUI–epoxy–SiO$_2$ composites were improved due to the presence of epoxy resin and silica particles.

In the last few decades, hybrid epoxy compositions containing two different modifiers (one in a liquid state and another in a solid state) were prepared in order to improve the thermal and mechanical properties of brittle epoxides. The use of both modifiers may promote the simultaneous occurrence of two toughening mechanisms, providing a synergistic effect on the fracture toughness. Shetty and Rai toughened the epoxy resin (DGEBA) with hydroxyl-terminated PU elastomer and fly ash as well as with hydroxyl-terminated PU elastomer and silane coupling agent treated granite powder [245,246]. In both cases toughened composites exhibited enhanced properties in comparison to the neat matrix. Hausnerova and coworkers [247] modified epoxy resins with PU and nanoclay (MMT). The improvement of the impact strength and flexural strain at break was observed, that was explained by increased content of the polymer matrix as well as the formation of chemical bonds between hydroxyl groups of the epoxy resin and the isocyanate groups of PU. Composites containing epoxy resin modified with PU and reinforced with an organomodified MMT also exhibited enhanced mechanical properties without significant changes of the T_g [248].

4.6. Epoxy resins in anticorrosion protection

Steel and other metals must be protected against the corrosion processes that occur under normal environmental exposure. The traditional methods of corrosion protection for steel have involved treatment by chromates. However, since chromate and similar hexavalent

chromium compounds are toxic and carcinogenic, their use and waste are restricted by most environmental legislation. On the other hand volatile organic compounds (VOC) in coatings and other sources may cause smog formation. The proposed lower emission levels have been reached by the application of water-based solutions to corrosion prevention needs. Isocyanate cross-linking agents have been identified as being hazardous air pollutants (HAPs), thus it is more difficult to apply polyurethanes and some resin systems as protective coatings against corrosion [249]. Many other polymers form thin films that have good anticorrosion properties. many hybrid epoxy–silane coatings have been developed for improved corrosion protection of metallic surfaces [250,251]. Hybrid coatings made by the hydrolytic polycondensation of amino-functional carbosilanes and other reactive silanes show good protective properties. The silane modified polymer protective coatings help to solve the metal corrosion problems. Silane functionality is very useful in achieving of the improvement of the adhesion and mechanical properties of the chemically bonded corrosion resistant of the epoxy–silane coatings.

Trialkoxysilanes with general structure $X_3Si(CH_2)_nY$ and bis-alkylenesilanes with structures $X_3Si(CH_2)_nSiX_3$, where X and Y represent a silicone ester and organofunctional group, respectively, have been applied to the need for "green" technology in the metal-finishing and the adhesive industries. Thicker films formed of products of the hydrolytic polycondensation of reactive silanes are usually too brittle, and the stability of the solutions used to deposit such layers are relatively poor. Several alternative methods have been attempted, starting with the inclusion of additives for the formation of the silane films anchored onto surfaces of nanosized fillers, and finishing with the modification of silane technology with conventional paint methodology. Chemically resistant epoxy–siloxane hybrids were introduced in the mid-1990s [252]. They were formulated from aliphatic epoxy resins, silicones and aminosilanes. The coating can be applied by brush, roll and airless or conventional spray to sand blasted steel, hand or power tool cleaned, rusted steel, a variety of organic primers and properly prepared, previously painted surfaces. The first commercially successful epoxy–siloxane hybrid was developed to improve the weathering resistance of epoxide without compromising corrosion or chemical resistance. On exterior exposure, the conventional epoxy coatings exhibit chalking and color fade and loose most of their gloss in three to six months. The epoxy siloxane hybrids showed about the same resistance to corrosion as the epoxy–polyamide, but exhibited significantly better resistance to acid exposure and accelerated weathering (QUV-B) under UV irradiation. The single coat of epoxy–siloxane provided comparable resistance to corrosion and better resistance to weathering compared to the two-coat epoxy–urethane systems. However, high crosslink density and shrinkage of chemical resistant epoxy–siloxane hybrids may result in cracking, delamination or debonding from concrete, particularly at high thickness. The use of elastomer modified epoxy–siloxanes have greatly reduced this problem [253,254].

Hybrid epoxy–silane coatings are most often applied for steel protection [147,158,168,255]. For example, materials prepared by a sol–gel/amine cure reaction of GPTMS were used as the matrix in coatings [256]. The silane precursor molecule (GPTMS) has both epoxy and silicon alkoxide functionality and so it can form interlinked inorganic–organic networks. Diethylenetriamine (DETA) was used as curing agent and formed the organic networks with the different ratios of amine to epoxy groups. These materials were cured at room temperature (RT) or at 150 °C. The structures of the hybrid systems were studied by Raman, FT-IR and ^{29}Si- and ^{13}C-MAS NMR spectroscopies. It was shown that the formation of the two kinds of networks did not occur independently and the rate or extent of organic cross-linking has a direct effect on the extent of the inorganic network formation, and vice-versa. Prehydrolysis of GPTMS with a stoichiometric amount of acidified water left the epoxy groups intact. DETA simultaneously opened epoxy rings and catalyzed silanol condensation to form the organic and inorganic networks at RT. The increase of the concentration of DETA increased the organic network formation [256]. The inorganic network consisted mainly of branching siloxane units $MeSiO_{1.5}$ (T_3) and was substantially formed at RT. Curing at 150 °C helped formation of both networks. The use of a low concentration of DETA resulted in an incomplete organic network at RT and there was sufficient freedom for the inorganic network to form. Thus, low DETA formulations required thermal curing to complete the organic network, while a high concentration of DETA resulted in a more complete and highly cross-linked organic network that constrained and inhibited formation of the inorganic network [256].

The steel corrosion was suppressed in both hot and humid conditions by the addition of silane coupling agents: (N-2-aminoethylaminopropyl)trimethoxysilane (AAPS), GPTMS, and bis[3-(trimethoxysilyl)-1-phenylpropyl-] tetrasulfide] (BTMSTS) to epoxy-coated steel as a primer. The silane coupling agents and epoxy were coated onto the steel surface using the solution casting method. The epoxy–AAPS–steel system demonstrated the best corrosions protection capability. AAPS formed the infinite siloxane network, that was thermally stable at elevated temperatures and resistant to water diffusion into the interface between coating material and steel. In the case of AAPS, FeOOOSi linkages onto the steel surface were formed, through a chemical reaction between the SiOOH and FeOOH groups. The epoxy–GPS–steel and epoxy–BTMSTS–steel systems showed lower corrosion protection capability than the epoxy–AAPS–steel system, due to different functional groups. The epoxy–AAPS–steel system (AAPS:epoxy = 6:4) suppressed steel corrosion at 400 °C for 10 minutes in air, and for 5 days at 60 °C in 100% relative humidity [256].

Polymer coatings have been used against corrosion and fouling of steel surfaces, ship bottoms, storage tanks and surface of pipelines. Another serious problem in the marine industry is biofouling, therefore the use of antifouling paints on the hull of ships is widely utilized. For the past 40 years, mainly copper and tributyltin (TBT) compounds have been used as antifouling coatings. Recently

some biocides such as lead, copper, arsenic, mercury and their organic derivatives have been restricted due to the environmental risks. Apparently, non-toxic foul-release paints, containing any heavy metals, are being applied as substitutes of TBT. Kumar and Sasikumar [73] elaborated nanocoatings from DGEBA as based material, tris(*p*-isocyanatophenyl)thiophosphate (DESMODUR) as the modifier, and POSS–NH$_2$ as nanoreinforcement, cured with polyamido-imidazoline and polyamidoamine. It was observed that the molecular structure of curing agent as well as the nanoreinforcing effect of POSS–NH$_2$ significantly affected the corrosion and fouling protection behavior. On some coating systems an impedance value of $10^9 \, \Omega \, cm^2$ even after 30 days of immersion was retained, indicating deteriotation. The synergistic effect of the curing agent and reinforcing effect of nanofillers toward corrosion resistance and inhibition of bacterial adhesion on such coated panels was also noticed [73].

Liu and coworkers [257] used ultrafine glass fibers (diameter 10 μm, length 50–80 μm), treated with (3-methacryloxypropyl)trimethoxysilane, in order to achieve corrosion protection of epoxy coatings. The addition of 10%, 20%, 30% of ultrafine glass fibers caused an increase of hardness and adhesion of the filled epoxy coatings by 67%, 87%, 200% and 21%, 39%, 40%, respectively, as compared to the properties of pure coatings. However, the anticorrosion properties of the coatings containing high content of ultrafine glass fiber decreased with respect to the neat coatings properties.

The epoxides are quite often used as anticorrosive coatings, especially due to their good chemical resistance and strong adhesion to metals. Decreased permeability of corrosive reagents (e.g., O$_2$ and H$_2$O) through coating-membranes also affects corrosion protection. The protective properties (vapor and gas permeability) of polymer–clay nanocomposite materials (PCNCs) were studied by Yeh et al. [258]. PCNCs were prepared from the epoxy resin (DGEBA), modified by siloxanes and montmorillonite clay (MMT); 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane was used as the curing agent. Nanoclay layers dispersed into the siloxane-modified epoxy matrice significantly increased the diffusion time for oxygen and water and the gas–vapor barrier of the coating. PCNCs had many predominances over typical epoxy resins: moderate glass transition temperature (T_g), higher tensile strength, lower cure shrinkage, and lower water absorption [258]. The effectiveness of the organic coating relied primarily on the interfacial adhesion strength between metallic surface and polymeric coatings. The proper corrosion inhibitors are usually expected to extend the service life of steel. Therefore, various silane coupling agents have been used as primers for increasing the corrosion protective effect of pure polymer coatings, due to the enhancement of interfacial adhesion strength between metallic surfaces and polymeric coatings. Yeh and coworkers [259] prepared anticorrosive coatings by the sol–gel process of DGEBA and GPTMS and evaluated their corrosion protective effect on the surface of steel. The enhancement of corrosion protective effect of epoxy–silica coatings was explained due to the increase of adhesion strength and surface hydrophobicity of hybrid sol–gel coatings on

steel coupons with respect to the neat epoxy resin. During the sol–gel process, through the hydrolysis and condensation reaction metal alkoxides form a condensed film as barrier layer on the metal substrate. Organofunctional alkoxysilanes were frequently used as sol–gel precursors as the adhesion promoters between polymer coatings and metallic surface. Better corrosion protection efficiency was observed with the use of TEOS or TMOS in comparison with pure polymer coating [259].

Two-part epoxy–siloxane anticorrosion coatings were also obtained from epoxies and (3-methacryloxypropyl)trimethoxysilane and (3-glycidoxypropyl)trimethoxysilane. (Aminopropyl)trialkoxysilanes served both as hardeners, reacting with the epoxide group to initiate cross-linking, and as the coupling agents to enhance adhesion of hybrid polymer resin to the metal surface [260,261]. Polymeric coatings based on epoxy–silicone–polyamide resins two-pack system, containing ordinary Portland cement or fly ash as extenders and titanium dioxide and zinc phosphate as main pigments, showed good anticorrosion properties on steel rebars in concrete [262].

Compositions, containing non-aromatic epoxides, polysiloxane ingredients, amine hardeners, and organotin catalyst, in their cured stage formed non-interpenetrating polymer network, useful as protective coatings that exhibit excellent weatherability in sunlight and superior chemical and corrosion resistance [263]. Compositions of epoxy resins with aminfounctional silanes used in combination with OH-terminated diorganosiloxanes gave resilient films with good freeze-release properties and improved abrasion resistance [264]. Sprayable, trowelable epoxy polysiloxane based coatings and flooring compositions showing extraordinary chemical, corrosion and impact resistance after curing and excellent weatherability in sunlight, were made of non-aromatic epoxy resins, polysiloxanes, trialkoxysilanes and difunctional aminosilane hardener and organotin catalyst [265]. Low-viscosity paint compositions were prepared from non-aromatic epoxy resins, polysiloxane and (glycidoxypropyl)trialkoxysilane or [(epoxycyclohexyl)ethyl]trialkoxysilane. The latter trialkoxy–silane improved paint adhesion and reduced the viscosity of the paint [266]. The useful material for anticorrosive coatings was prepared in reaction of cyclotetrasiloxane, having two aminopropyl groups, with novolac epoxy resin and cured with *m*-phenylenediamine (MPDA) [267]. For epoxy–silicone films a so-called hair pinning effect was observed, in which siloxane chain segments migrate to, and become "pinned" at the coating surface [268].

IPN polymer networks were obtained from mixtures of epoxy resins and CFS bearing the amino and epoxy groups by simultaneously proceeding reactions of curing oxirane rings with amine groups and the hydrolytic polycondensation of silanes. Coatings containing the IPN's exhibited superior thermal stability, greater chemical, weathering and corrosion resistance than coatings containing the neat epoxy polymer. They can be used for anticorrosion protection of steel constructions of chemical processing plants, oil refineries, coal-fired power plants offshore drilling platforms, and internal surfaces of tanks used in transport of chemicals [269].
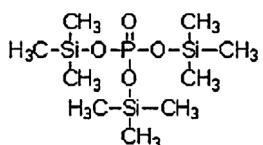
Fig. 29. The chemical structure of tris(trimethylsilyl)phosphate (TMS-Ph). Reprinted (adapted) with permission from [273]. Copyright 2011, Elsevier.

The epoxy–silica hybrids, prepared from silane-functionalized oligomers of DGEBA resin with different molecular weights, modified with molybdate anions, were also found to be useful as anticorrosion protective coatings. Many benefits derive from the incorporation of molybdate anions within the siloxane network of epoxy–silica hybrids, particularly when the molybdate species were added in the form of an amine salt obtained from the reaction of the amine hardener and molybdic acid. The doping of the siloxane network with molybdate species not only densified the network of the inorganic domains, but also brought about a increase in T_g of the organic phase [168].

Khramov and coworkers prepared hybrid organic–inorganic coatings in sol–gel processes: (1) from epoxy resins and aminosilanes [270] or (2) by hydrolysis and condensation reactions of a mixture of (diethylphosphonatoethyl)triethoxysilane (PHS) and TEOS with different molar ratios in ethanol-water solution [271]. These organosilicate barrier coatings had improved adhesion and corrosion resistance, through the interactions of the phosphonate groups with the surface of magnesium and its alloys. The obtained coatings showed improved properties in comparison to products previously described in the literature, however their performance was only tested for two weeks under mild conditions. Lamaka et al. [272] synthesized organic–inorganic sol–gel coatings by copolymerization of epoxy–siloxanes with titanium or zirconium alkoxides. Addition of tris(trimethylsilyl)phosphate (TMS-Ph) (Fig. 29) caused significant improvement of the corrosion resistance of the magnesium alloy during relatively short immersion time (only one or two weeks).

Some anticorrosion formulations did not contain epoxy components. The protective properties of coatings prepared from bis[triethoxysilylpropyl]tetrasulfide (BTESPT) and modified with cerium or lanthanum nitrates were studied by Montemor et al. [274]. Zhang et al. [275] elaborated a novel sol–gel process, using appropriate additives for dispersion and stabilization of precursors, e.g., inorganic cerium salts. The sols with a controlled pH were useful for a protection of magnesium alloys, although the improved corrosion resistance was tested only within a few-hour time. Very recently Kartsonakis et al. [276] introduced cross-linked epoxy nanocontainers, with addition of cerium molybdate in the organically modified silicates as a corrosion inhibitor.

The newer hybrid epoxy–silane coatings were modified with silane coupling agents (APTES, APTMS, GPTMS and TMS-Ph), as functional additives to improve their performance and durability, and especially to increase the corrosion protection of magnesium materials. The coating
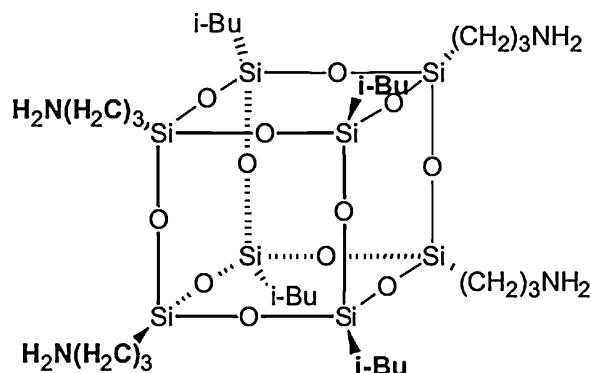
Fig. 30. The molecular structure of an isomer of tetra(3-aminopropyl)tetraisobutyloctasilsesquioxane (AP$_4$IB$_4$-POSS). Reprinted (adapted) with permission from [278]. Copyright 2011, Elsevier.

solution consisted of three main ingredients: silane, epoxy component (DGEBA resin), and diethylenetriamine (DETA). It was shown that the corrosion resistance and the barrier properties of such coatings depend on the chemical structure of the above carbofunctional silanes [273].

Other polysiloxane-modified epoxy coatings (CPSA) were prepared using the mixture of poly(aminopropyl, methyl)siloxane (PAPMS) and N-(2-hydroxyethyl)ethylenediamine as curing agents and cardanol as a compatibilizer. The PAPMS oligomer was prepared by the controlled hydrolytic polycondensation of (3-aminopropyl)(dimethoxy)methylsilane. For comparison the conventional epoxy resins were also prepared by curing with a commercial phenalkamine (PECA). The anticorrosive performances of the CPSA- or PECA-based epoxy coatings were thoroughly examined by electrochemical impedance spectroscopy (EIS), salt fog tests, and immersion experiments in acid (25 wt.% H_2SO_4), alkali (25 wt.% NaOH), and saline (3 wt.% NaCl). Cardanol strongly improved the miscibility of CPSA with epoxy resins. Polysiloxane-modified (CPSA-based) epoxy coatings had much better corrosion resistance than conventional (PECA-based) epoxy coatings [277].

Jerman et al. [278]. evaluated the influence of the addition of a mixture of POSS compounds substituted equally by 3-aminopropyl and isobutyl groups (AP$_4$i-B$_4$-POSS) (Fig. 30) on anticorrosion properties of sol–gel coatings prepared from (3-glycidoxypropyl)trimethoxysilane (GPTMS).

AP$_4$i-B$_4$-POSS functionalized with four amino groups enabled cross-linking with the epoxy groups of GPTMS. Additionally, GPTMS molecules reacted among themselves through hydrolysis and condensation processes of trimethoxysilane groups when catalyzed by a 0.1 M KF solution. The results of Raman and IR measurements revealed that a molar ratio of GPTMS:H_2O = 1:3 was more beneficial, than a molar ratio of 1:1.5 for the preparation of sol–gel coatings. The anticorrosion properties of the mixed GPTMS/POSS coatings deposited on aluminum alloy were tested using potentiodynamic electrochemical measurements and a salt-spray chamber test. It was found that the mixed GPTMS/POSS coatings showed improved corrosion protective properties in comparison with either pure GPTMS or POSS coatings [278].

BPA based epoxide resin

Epoxy phosphate
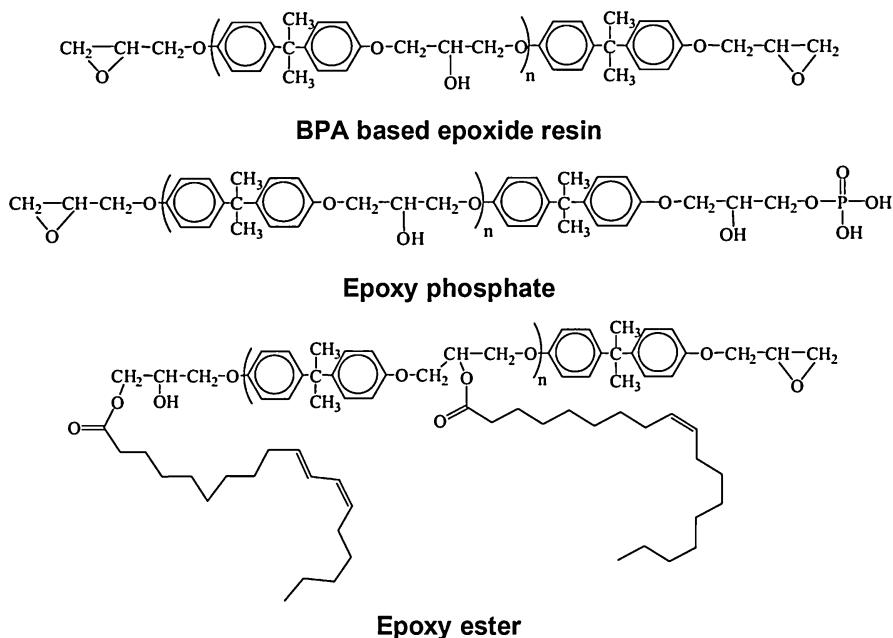
Epoxy ester

Fig. 31. The chemical structures of epoxide derivatives. Reprinted (adapted) with permission from [279]. Copyright 2012, Elsevier.

Telechelic resins with reactive epoxy phosphate and epoxy ester end groups were synthesized from bisphenol-A (BPA) epoxide (Fig. 31) [279,280]. The bisphenol-A based epoxide, the epoxy phosphate, and the epoxy ester were all modified with TEOS oligomers that were prepared through the hydrolysis and condensation of TEOS monomer with water under acidic condition. The modified epoxides (Fig. 32) were cast on steel substrates and thermally cured with a melamine-formaldehyde resin. Viscoelastic properties of the hybrid systems were also evaluated as a function of polysilicate content. The coating performance of the modified epoxides was evaluated by pencil hardness, crosshatch adhesion, reverse and direct impact resistance, mandrel bending, and pull-off adhesion. Corrosion performance was evaluated via salt spray (fog) test for 264 h. Salt spray analysis revealed that inorganically modified epoxies provided improvement over the unmodified epoxy resins with respect to both corrosion resistance and adhesion to steel substrates [279].

Protective coatings are always at the risk of being damaged or scratched at a micro-level during transportation, installation and service. The self-healing concept was successfully proved to autonomously repair microcracks in the coating, and micro-capsulation was the most sufficient and widely used way among a number of approaches for self-healing materials development. Yang et al. [281] used 1*H*,1*H*,2*H*,2*H*-perfluorooctyl triethoxysilane (POTS) in microcapsulated form as the healing agent. POTS microcapsules were incorporated into the epoxy resin and coated on a steel substrate, providing a corrosion resistant organic coating. The corrosion prohibition functionality was realized by the self-healing mechanism of encapsulated POTS, that hydrolysed with water upon being scratched.

4.7. Epoxy resins modified with silanes and silicones in combination with other polymers

Liu et al. [23,24] modified the epoxy resin (DGEBA) through the sol–gel process, using alkoxysilane-functionalized polycaprolactone (PCL–TESi) [22] and a mixture of polycaprolactone and PDMS, with terminal [(trialkoxysilane)propyl]urethane groups (PCL–PDMS) in the presence of polyamidoamine used as the curing agent. The toughness, thermal stability, chemical resistance and mechanical properties of the modified systems were greatly improved due to the formation of Si–O–Si networks in the epoxy matrix. Addition of 3-triethoxysilyl-*N*-(1,3-dimethylbutylidene)propylamine (Fig. 33) increased the compatibility between the PCL–TESi and DGEBA [22].

Epoxy resins modified with silyl-terminated polycaprolactone showed the crucial improvement of the mechanical properties: impact resistance, elongation and peel strength, fracture energy. These properties could be also easily taylored by adjusting the ratio and selection of the silylated elastomer and the epoxy resin [23,282,283].

Organic–inorganic hybrid materials, combining the desirable properties of organic polymers (toughness, elasticity) with those of inorganic solids (hardness, chemical resistance) have been recommended as novel functional materials. Up to now, most of the organic–inorganic hybrid materials are epoxy–silica–polyacrylates and epoxy–polyacrylates [171,284–286]. Acrylic resins have hydrolytic, light, and oxidative stability. The epoxy resins have functional epoxy groups and have subsequent excellent characteristics, such as heat resistance and good adhesion. Silica materials have excellent light, heat and water resistance. It was expected that increased interfacial interactions through hydrogen bonds or covalent bonds

TEOS modified epoxide

TEOS modified epoxy phosphate

TEOS modified epoxy ester
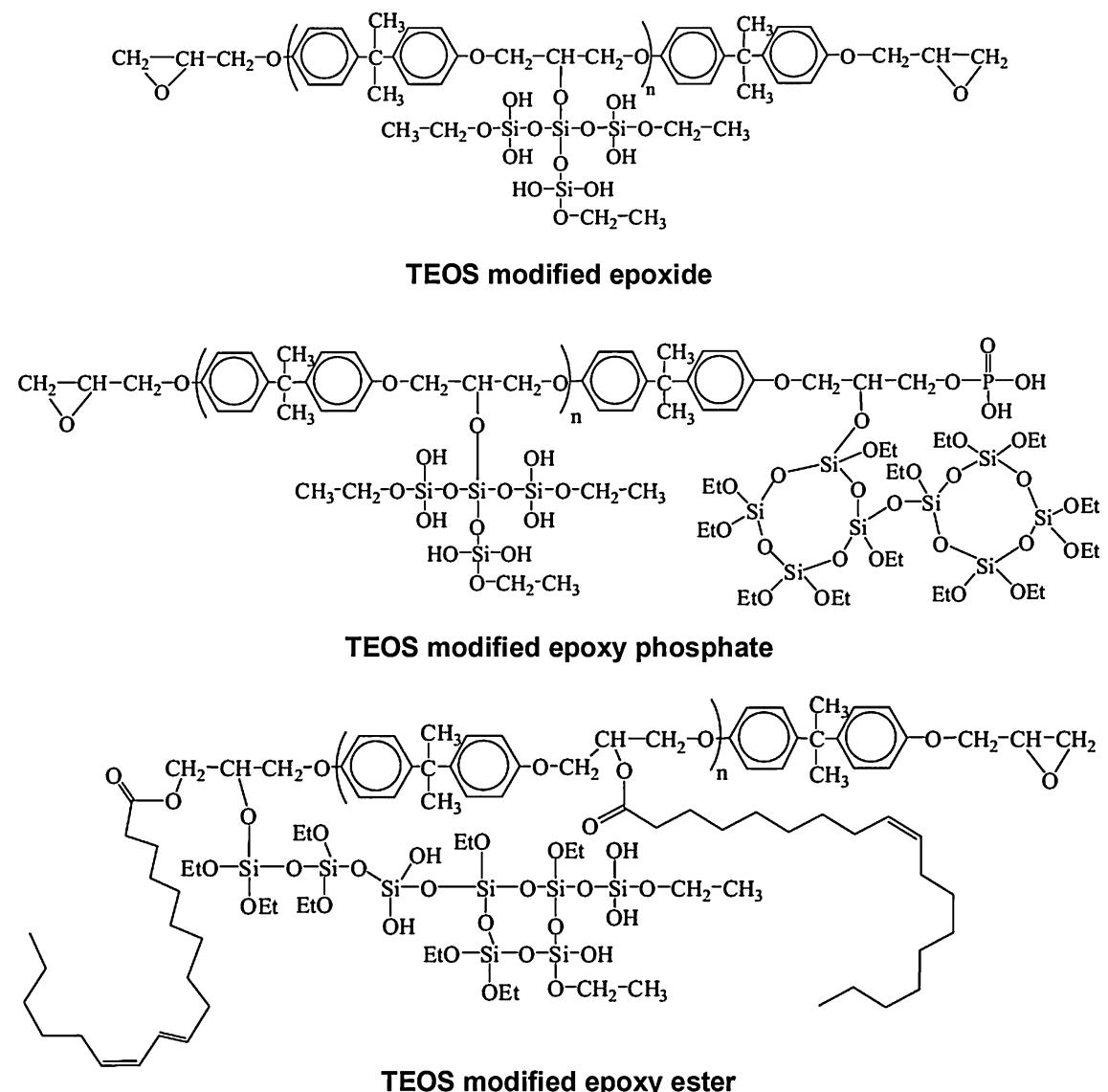
Fig. 32. The chemical structures of epoxies modified with TEOS oligomers. Reprinted (adapted) with permission from [279]. Copyright 2012, Elsevier.

between the organic and inorganic phases, will result in superior properties compared to classical composites. Wan et al. [151] prepared an organic–inorganic epoxy–silica–acrylate hybrid coating by radical solution copolymerization and sol–gel process of a mixture of (methacryloxypropyl)trimethoxysilane capped acrylic resin, epoxy resin and TEOS. This composite, cured by (aminopropyl)triethoxysilane, formed transparent hybrid coatings with a homogeneous distribution of nanosized inorganic particles in the polymeric matrix. With increasing of TEOS content (>20%) the transmittance in the visible region and the yellow index (YI) of the hybrid

$$Me_2C=N(CH_2)_3Si(OEt)_3$$

Fig. 33. The chemical structure of 3-triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine.

coatings after UV irradiation decreased, while the onset decomposition temperature and maximum weight loss temperature increased.

An interesting method for the preparation of coatings, in particular on glass substrates, reported Hariri et al. [92], who developed a "one-pot" preparation of non-aqueous dispersion (NAD) [287–289] in a polymerizable liquid medium, containing two monomers: epoxy functionalized PDMS (PDMS–diglycidylether DGE) and vinyl acetate (VAc). Vinyl acetate was selectively polymerized in the presence of a free-radical initiator. That led to the formation of a NAD because the poly(vinyl acetate) (PVAc) was insoluble in PDMS–DGE. In a further step, after application of the NAD on the substrate, the PDMS–DGE continuous phase could be polymerized by UV initiated cationic polymerization to obtain a polymeric two-phase material, without any solvent emission.
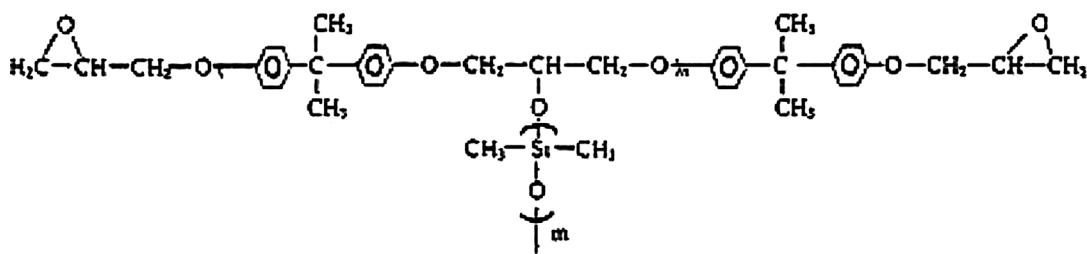
Fig. 34. The structure of the silicone rubber–epoxy copolymer. Reprinted (adapted) with permission from [301]. Copyright 2003 Wiley Periodicals, Inc.

Blending or adding thermoplastic polymers to the thermoset epoxy resin were often used to toughen epoxy materials. Elastomers (carboxy-, amine-, or hydroxyl-terminated acrylonitryle butadiene rubbers), functionally terminated acrylates, polyurethane, and others, were mostly used for this purpose, due to their improved toughness and good solvent resistance [290–293]. Silicone rubbers, especially PDMS with its attractive properties including high chain flexibility, high thermal and oxidative stability, low T_g and good hydrophobic behavior, could be an effective modifier for epoxy resins. However, because of the poor compatibility between soft segments of siloxane chains and polar hard segments in epoxy resins, pure PDMS had been rare used as the toughening agent. These materials, that usually exhibited separate T_g values due to the thermodynamic incompatibility, were either macroscopically immiscible or migrated from the cross-linked matrix during curing procedure in the conventional introducing of siloxane moieties into polymers through blending methods [294–296]. To overcome this limitation and improve the interaction between PDMS and epoxy matrices have been reported the use of silane coupling agents [297,298] or chemically incorporating PDMS into the main chain of epoxy to form the interpenetrating network [294,299].

CFPS with shorter chain lengths are more reactive and miscible with epoxy resins, and are suitable for modification of the bulk properties of the epoxy matrix such as thoughness and impact resistance. Compositions with longer siloxane chains decrease the miscibility with epoxides and the properties of the modified resins were governed less by the terminal organofunctional groups and more by the PDMS portion of the molecule. In these cases, the silicones acted mainly as the surface modifiers, providing lubricity, low surface energy and water repellency [268].

Tetrafunctional epoxy resins with a softer aliphatic backbone, cured by 4,4'-diamino-diphenyl sulfone in the presence of curing accelerator: triphenylphosphine, were modified with amine-terminated PDMS by Hsieh et al. [300]. The PDMS-modified epoxy resins showed higher early cure reactivity, a lower crosslinking density,

and effectively reduced the stress by creating dispersed phases of sea-island dissipation morphology. A novel methodology for preparation of the interpenetrating polymer networks (IPNs) between the epoxy resin (DGEBA) and PDMS proposed Li and coworkers [138]. Partially crosslinked vinyl-terminated PDMS with PDMS containing Si—H groups was mixed with DGEBA, modified silica, and anhydride curing agent. The modified silica played a double role: as the curing agent with DGEBA and as the compatibilizer between DGEBA and PDMS, inhibiting serious phase separation of the two components, thus ensured the formation of the IPN structure. Introduction of silica to form the epoxy–silica hybrid through the sol–gel process also improved the properties of the epoxy resin such as toughness, impact strength, and thermal degradation.

Properties of liquid silicones were modified by addition of the epoxy resin (EP) and polyurethane (PU). The mechanical properties of composites based on a silicone rubber (SR), PU, and EP with different blending proportions were studied by Chiu et al. [301]. The PU structure consisted of polybutyleneadipate, butanediol, and toluene-2,4-diisocyanate units. The intermolecular interaction of the three-phase polyblends was studied by dynamic mechanical analysis. Reactions between the SR, PU, and EP produced a crosslinked network (Figs. 34 and 35).

Mechanical properties, including the tension, compression, shear, and tear performance, were measured. From the relationship between the intermolecular interaction and mechanical properties, it was found that the structure of the three-phase blends was influenced by the reaction between silicone and PU, silicone and EP, and PU and EP, affecting the crosslinking density and the IPN structure. Thus, the dominant three-phase mechanical properties were closely related to the IPN structure [301].

The mechanical properties of IPN's based on epoxy resins and 5–20 wt.% of hydroxyl terminated polydimethylsiloxane (PDMS) were investigated by Abdelrazaq and coworkers [302]. The main objective of this study was to use PDMS as an impact modifier for epoxy resins. New IPN's between epoxy resins and different weight percentage of PDMS were prepared in the presence of TEOS as
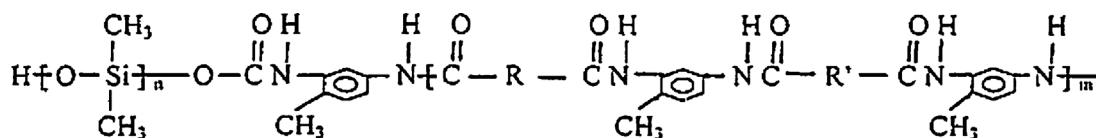
Fig. 35. The structure of the silicone rubber-PU copolymer [301]. Reprinted (adapted) with permission from [301]. Copyright 2003 Wiley Periodicals, Inc.
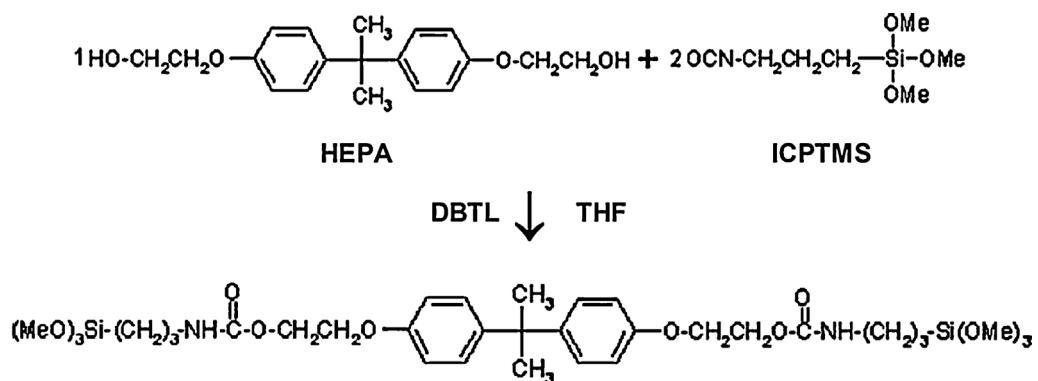
Scheme 41. Formation of trimethoxysilane-terminated HEPA-urethane. Reprinted (adapted) with permission from [303]. Copyright© 2006, Elsevier.

the crosslinking agent for PDMS and triethylenetetraamine (TETA) as the hardener for epoxy resin. The tensile strength (TS) of the epoxy–PDMS IPN decreased with increasing content of PDMS in the IPN prepared, while the elongation at break (E_b) increased. On the other hand, the storage modulus E', loss modulus E'', and complex modulus E^* of an epoxy resin modified with PDMS decreased with increasing weight percentage of PDMS in the network structure. PDMS acted as a potential toughening for epoxy resin, with the toughness of the epoxy resin increased by the addition of PDMS with the optimum toughness obtained with the addition of 5 wt.% PDMS. Results of DMA showed the increase in flexibility caused by the addition of PDMS. Stiffness of the resultant material was also temperature sensitive. All the DMA measurements were sensitive to the frequency of oscillation [302].

UV-curable, organic–inorganic hybrid coatings based on a UV-curable epoxyacrylate resin (EA) and (methacryloxypropyl)trimethoxysilane (MAPTMS) were prepared by the sol–gel method. 2,2′-Bis(4-β-hydroxyethoxy) phenyl propane (HEPA) was modified by the coupling agent, (3-isocyanatopropyl)triethoxysilane (ICPTMS), in the presence of dibutyltin dilaurate, to improve the compatibility of the organic and inorganic phases (Schemes 41 and 42) [303]. These composites were applied on aluminum panels and cured by UV light, giving a hard and clear coating with a good adhesion. The pendulum hardness, cross-cut adhesion, gloss and the impact strength of the coatings increased systematically with increasing MAPTMS and trimethoxysilane terminated HEPA urethane (TMSHU) content in the hybrid mixture. The enhancement of the physical and mechanical properties was correlated with an increase in cross-linking density of the system. The morphology studies indicated the presence of a hybrid composite with nanoscale dimensions. The thermal stability of nanocomposite hybrids was also higher than that of the pure epoxy acrylate resin [303].

The transparent epoxy resins obtained by anhydride curing of DGEBA were commonly used in the light emitting diodes (LED) encapsulation [119]. Hydrogenated
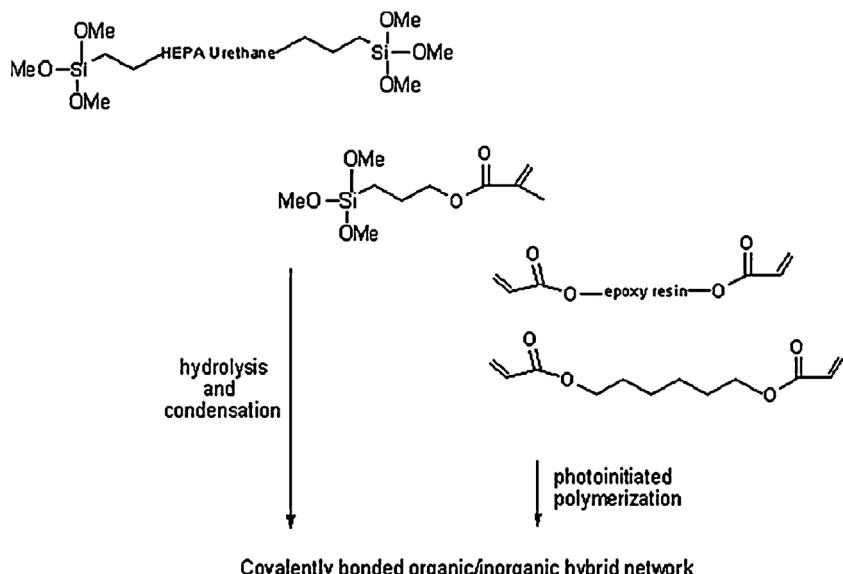
Scheme 42. The illustration of the formation of an organic–inorganic hybrid coating. Reprinted (adapted) with permission from [303]. Copyright© 2006, Elsevier.
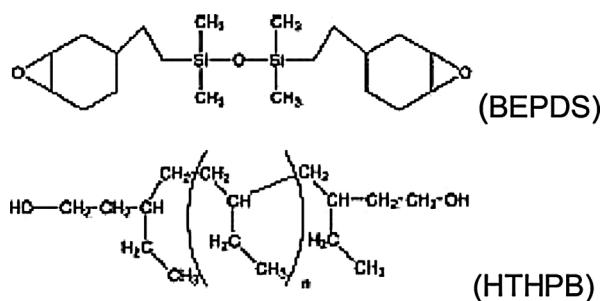
Fig. 36. The chemical structures of BEPDS and HTHPB. Reprinted (adapted) with permission from [120]. Copyright 2008 Wiley Periodicals, Inc.

bisphenol A glycidyl ether [304] or epoxy siloxane hybrid [305,306] were used for photothermally stable materials. The epoxysiloxanes were expected to improve photothermal stability, but the hard and brittle nature caused the biggest difficulties in the encapsulation. The epoxysiloxane monomer with longer siloxane segment was expected to improve both flexibility and photothermal discoloration. Various stress modifiers can also control the crosslink density of epoxy thermosets, i.e., hydroxyl-terminated liquid rubbers are well known stress modifiers of epoxy resins [307,308].

Morita et al. [306] demonstrated LED encapsulation by novel siloxane monomers (Fig. 36) of 1,3-bis[2-(3-(7-oxabicyclo[4.1.0.]-heptyl)-ethyl]tetramethyldisiloxane (BEPDS) with hydroxyl-terminated hydrogenated polybutadiene (HTHPB). With increasing rubber concentration significant flexibility improvement of the epoxy siloxane hybrid was observed and the LED encapsulation with this material demonstrated no cracks when the HTHPB content was at least 30 wt.%.

(3-Aminopropyl)$_8$Si$_8$O$_{12}$ was used as the additive to improve the thermooxidative stability of epoxy resin and cyanate ester systems [309,310]. Several thermosetting epoxy resins were applied for anisotropic conductive adhesive film materials (ACAF) [311], because the thermosetting epoxy adhesive materials are very stable at high temperature and give low contact resistance. Liquid crystal display (LCD) panels became very important components for mobile electronics and a high-density interconnector material, ACAF is the most popular material for attaching the tape-carrier packages and the tape automated bonding and chip-on-glass packages to the LCD panel. ACAF, generally called "z-direction conductive adhesive materials" is composed of an adhesive thermoset polymer matrix and fine conductive fillers, such as metallic (Ni) particles or metal (Ni/Au)-coated polymer balls, while the electrical isolation in the x–y direction is maintained. For the adhesive polymer matrix, the mixed resin of thermoplastic elastomer and thermosetting epoxy polymers used to provide electrical insulation, to protect the metallic contacts from mechanical damage, and to provide stable adhesion. Kim et al. [312] reported the thermoset type ACAF, composed of the epoxy resin DGEBA, carboxylated acrylonitrile butadiene rubber (XNBR), microcapsulated imidazole as the curing agent, an epoxysilane coupling agent, and a conductive filler composed of Ni/Au coated polymer beads.

Durability tests under the condition of 80 °C and high humidity (85% RH) and the thermal shock test between −15 and 100 °C showed their excellent performance. The strength of the adhesion after cure was enough to sustain good conduction between a glass and Cu-patterned polyimide film.

Poly(methyl methacrylate) (PMMA), polycarbonates and epoxy resins are most often used polymers in optical goods [313]. Optical interconnects are very important in recent advances in electronics. They are especially useful for communicating information because they offer higher frequency, shorter wavelength and greater photon energy in comparison to electronic interconnections. Optical waveguides commonly consist of a dielectric material having a high refractive index surrounded by the lower refractive index cladding material. Light waves are then guided by total internal reflection, due to the waveguide core having the refractive index higher than that of the surrounding material. The use of polymeric optical waveguides is one way to avoid some problems associated with common electronic data transfer. According to Woods et al. [314] an (epoxy)propoxy-terminated poly(dimethyl, diphenylsiloxane) copolymer is suitable for applications in the fabrication of optical waveguides by two photon induced polymerization (TPIP) on printed circuit boards (PCB). This polysiloxane with epoxy functionality was cured with an aminopropyl disiloxane crosslinker forming the matrix material. Three, different high refractive index acrylate monomers (benzyl acrylate, phenyl acrylate, and 1,3-butanediol acrylate) were used to form the polymeric network with higher refractive index than that of the matrix. This material fulfilled a number of requirements, including a good refractive index contrast between the matrix material and inscribed wave-guide, full flexibility and the high thermal and chemical stability. Waveguide bundles were successfully fabricated on specially designed PCB substrates to produce optical interconnectors.

Aligned nanofibers, based on poly(butylene terephtalate) (PBT) and polyhedral (epoxycyclohexyl)isobutyl polyhedral oligomeric silsesquioxane (POSS), were prepared from polymeric solutions at different POSS contents (namely 0, 3, 6, and 10 wt.%). Nanofibers based on PBT/POSS system were prepared by electrospinning and fully characterized. The presence of POSS affected not only the fiber alignment but also the orientation of crystallites during the annealing process [315].

4.8. Antimicrobial coatings from silane modified epoxy resins

Bacterial infections are serious problems around the world. The first step of the development of an infection is the adhesion of bacteria to a biomaterial surface, affording possibilities for its subsequent propagation. One way to prevent bacterial contact with substrate is disintegration of the microorganism to avoid adhesion. Another way is the invention of effective biocidal surfaces. The use of epoxy resing hybrids for such a purpose requires the introduction of a suitable component, providing some flextibility as well as a hydrophilic character. Among various polymers, polydimethylsiloxane chain provides a

component to introduce flexibility, but its hydrophobic character of polysiloxanes is commonly known. Nevertheless, the incorporation of hydrophilic groups into PDMS can modify the hydrophobic properties. The hydrophilic, fungicidal and bactericidal properties of quaternary ammonium salts (QAS) known for a half a century make them a candidate to modify PDMS for use in a biocidal surface [316–321]. QAS compounds belong to the class of cationic disinfectants. An electrostatic interaction of QAS molecules with the cell wall enables their biocidal activity, with the lipophilic moiety present in the ammonium salts destabilizing the cytoplasmic membrane, leading to death of the bacteria cell. The PDMS–QAS polymers are used for finishing of textiles, in cosmetics and personal care [321]. The PDMS–QAS materials with a longer hydrocarbon chain at nitrogen exhibit biocidal properties destroying bacteria, fungi and algae. Wynne and coworkers [322] reported the PDMS–QAS epoxy systems as effective materials for antibacterial coatings with a low surface energy. They synthesized quaternary diglicidyl phenyl ammonium compounds that were reacted with diamino-substituted PDMS. The biocidal activity against both Gram-positive and Gram-negative bacteria of obtained materials were evaluated to show that the coatings eliminated up to 99.9% of pathogenic bacteria on the surface. They were capable of self-decontaminating in a variety of environments and were active for long time without the risk of leaching antimicrobial moieties, because the quaternary ammonium salt sequences are incorporated in the backbone of polymers.

5. Summary and conclusions

The addition of commercially available CFS, CFPS, silica, silicates and other fillers or nanofillers affects many properties of the modified epoxy resins. These additives limit, to a large extent, disadvantages of epoxy thermosets. In most cases the addition of CFPS in combination with other elastomeric polymers affects a decrease of the glass temperature of crosslinked materials. This phenomenon is very important for the fabrication of epoxy composites and nanocomposites.

Hybrid epoxy–silicone materials are especially useful as protective coatings for the different metallic or architectural surfaces. Silicone components increase the weathering resistance since epoxy–siloxane coatings retain a gloss for a very long time and do not exhibit a chalking effect on exposure to sun light or moisture.

Anticorrosive coatings made of epoxy resins modified with CFS and CFPS show significantly improved durability and good adhesion to steel, aluminum and other metallic surfaces. They exhibit the significantly better protection against corrosion, thanks to decreased water absorption, as the result of the hydrophobic properties of siloxane components. The anticorrosive epoxy–siloxane coatings have excellent dielectric properties, that can be retained even in the presence of boiling water.

The addition of CFS or/and CFPS can decrease the viscosity of epoxy resins. making such liquid compositions useful for application as coatings, that after curing processes (very often without any emission of volatile organic compounds

to an atmosphere) give stable coatings with the improved abrasion resistance.

The effectiveness of CFS and CFPS in the manufacture of nanocomposites is commonly known. These additives avoid agglomeration of nanoparticles in polymer matrices and simultaneously promote better adhesion of epoxy resins to the nanofillers, confirmed by a huge number of literature reports concerning these applications in reactive silanes and siloxanes.

CFS and CFPS of the different chemical structures are also very useful as the additives, that (in most cases) stimulate the improved impact resistance, tensile strength, thermal stability and fire retardancy of epoxy resins, their composites and nanocomposites. The synergistic effect of CFS and phosphorous derivatives has been observed, e.g., in the increase of the limiting oxygen index (LOI) up to 44, in comparison with the LOI value ~24 for neat epoxy resins.

The usefulness of CFS and CFPS has been also observed in modifications of the properties of the compositions or blends of epoxy resins with other polymers: thermoplastics and elastomers. A number of chemical corporations (Dow Corning Corp, Wacker-Chemie, Evonik Industries, Momentive Specialty Chemicals, Shin Etsu and other companies) offer a range of conventional and special CFS and CFPS for various applications (adhesion promotion, surface modification, crosslinking, endcapping, radical grafting copolymerization, and compatibilization of materials). However, the relatively high cost of CFS and CFPS represent the main limitation in their universal applications.

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