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Modification of Thermoplastics with Reactive Silanes and Siloxanes

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1. Introduction

In a contemporary world goods made from plastics and other polymeric materials are applied in many areas of our life. Growing practical applications are mainly stimulated by better properties of modified polymers, in a comparison with the polymeric materials used so far. On a world polymer market a biggest production concerns thermoplastics, thus modification of their properties has become one of a most important research challenges in a field of a polymer chemistry and technology, and materials science as well.

Silicones (polysiloxanes) are a large and most important group of various inorganic-organic (hybrid) compounds and materials, composed of silicon and oxygen atoms in their main chains and organic substituents bound to silicon. Silicones play an important role among polymers with special properties, because they possess many unusual features. Even an addition of a very small amount of silicones causes a crucial improvement of properties of modified materials. Most importantly: silicones increase hydrophobicity and improve water resistance and thermal stability of many materials. Silicones exhibit excellent chemical, physical, and electrical properties. Most popular organosilicon polymers are polydimethyl-siloxanes (PDMS). Silicones are mainly applied as silicone oils, rubbers, and resins (Noll, 1968; Rościszewski & Zielecka, 2002). Similar positive effects on properties of polymers and other materials can be reached by the addition of reactive silanes, siloxanes, and silicates, which are also used very often in practice for the modification of polymeric and inorganic materials. An important practical meaning have also other organosilicon polymers (polysilanes, polycarbosilanes, polysilazanes, etc.), and many functional silanes with different chemical structures, containing reactive groups, mostly bound to silicon atom, but also quite often attached to carbon.

We observe a continuously growing interest in applications of reactive silanes and polysiloxanes in many different fields of science (with focus on materials science) and the chemical technology, and this is a subject of our review.

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2. Reactive silanes and siloxanes

2.1 Functional groups and reactive silanes in silicon chemistry

In organosilicon chemistry most important are following functional groups: ≡Si-Cl, ≡Si-OR, ≡SiOCOR (R – usually alkyl group), ≡Si-H, and ≡Si-CH=CH_2. They are present both in all kinds of organosilicon compounds and polymers and can be grafted on silica, silicates, and some inorganic fillers. Functional organic silanes include first of all: chlorosilanes, alkoxysilanes, and acetoxysilanes (e.g. dimethyldichlorosilane, methyltriethoxysilane, methyltriacetoxysilane, etc.), and different functional and carbofunctional silanes (Brook, 2000, Eaborn, 1960; Kricheldorf, 1996). Moreover very often are used inorganic chlorosilanes: silicon tetrachloride $SiCl_4$, trichlorosilane $HSiCl_3$, and dichlorosilane H_2SiCl_2, and silicate compounds: esters of silicic acid, and especially tetraethoxysilane $Si(OEt)_4$, tetramethoxysilane $Si(OMe)_4$, and tetracetoxysilane $Si(OAc)_4$. Chlorosilanes are produced on an industrial scale by Rochow-Miller process, and their fast reactions with alcohols (or metal alkoxides) and carboxylic acids lead to appropriate alkoxysilanes or acyloxysilanes, respectively.

2.2 Functional siloxanes and polysiloxanes

Siloxane oligomers (linear and cyclic) and polysiloxanes (silicones) are mainly prepared by so called a multistep "hydrolytic polycondensation" of chlorosilane monomers of different functionality. This step-growth process consists of elementary hydrolysis and condensation reactions:

$$\equiv\text{Si-Cl} + H_2O \longrightarrow \equiv\text{Si-OH} + HCl \quad (1)$$

$$\equiv\text{Si-Cl} + \text{HO-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + HCl \quad (2)$$

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + H_2O \quad (3)$$

Linear oligo- and polysiloxanes with diferent functional (α,ω-terminal or pendant) groups and functional cyclosiloxanes find many applications in further syntheses. These functionalities include most often silanol, chlorosilyl, hydrosilyl, vinyl, and allyl groups.

2.3 Carbofunctional Silanes (CFS)

Carbofunctional silanes (CFS), which are used for a long time in a processing of plastics may be considered as precursors of carbofunctional polysiloxanes. The carbofunctional silanes are compounds with a general formula $X_nSi(R'Y)_{4-n}$, where: R' – alkylene chain, Y – functional group, e.g. Cl, NH_2, NR_2, OH, OCOR, NCO, CH_2=CH, SH, and X – a functional group sensitive to hydrolysis (Cl, OR, OCOR). Alkylene chain R' is usually built of three methylene groups (Marciniec et al., 1990, 1992a, 1993; Chruściel et al., 2008a).

The carbofunctional silanes are usually prepared in a three step synthesis. In a first step a catalytic hydrosilylation reaction of allyl chloride with hydro(alkyl)chlorosilanes is carried out, in a second step – alcoholysis of addition products, and in a last step – substitution of chlorine atom in (chloropropyl)trialkoxysilane $Cl(CH_2)_3SiMe_n(OR)_{3-n}$ by a catalytic nucleophilic substitution - take place (Guliński et al., 2003).

2.4 Carbofunctional Polysiloxanes (CFPS)

Weak interactions between polysiloxane chains (through van der Waals forces) are responsible for poor mechanical properties of these polymers at room temperature, even in the case of PDMS with a very high molecular weights (Abe & Gunji, 2004). An improvement of mechanical properties of PDMS can be reached by addition of fillers (most often silica is used), by a dense crosslinking in the presence of peroxides, or by synthesis of siloxane-organic copolymers of different structures (block, segmented, or graft). Since both systems are thermodynamically non-miscible it is impossible to prepare siloxane-organic copolymers from (α,ω-dihydroxy) polydimethylsiloxanes, and it was necessary to use for this purpose α,ω-dihydro- or α,ω-divinylpolysiloxanes, but first of all to use the carbofunctional polysiloxanes (CFPS) (Chruściel et al., 2008b).

The general structure of carbofunctional polysiloxanes is presented on Fig. 1.

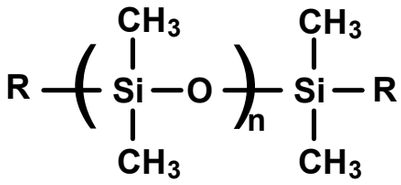
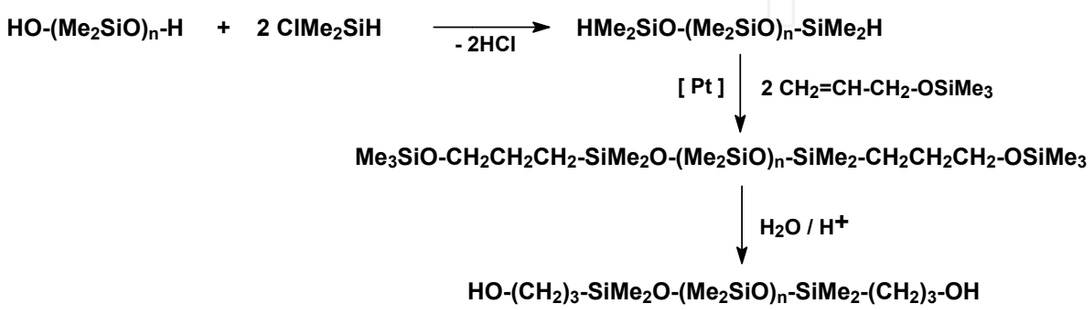


Fig. 1. The chemical structure of α,ω-dihydro-, α,ω-divinyl-, and the carbofunctional polysiloxanes (R = H, CH = CH_2, aminoalkyl, hydroxyalkyl, chloroalkyl groups, etc.)

2.4.1 Synthesis of CFPS

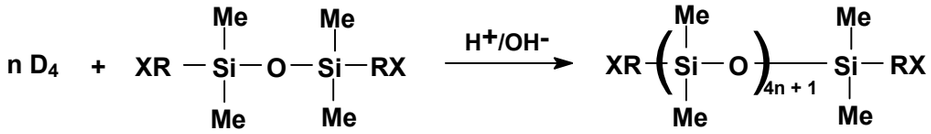
Macromolecules of the carbofunctional polydimethylsiloxanes (CFPS) are terminated with different functional alkylene groups. Most often on both ends of CFPS chains exist hydroxypropyl, aminopropyl, glicydoxypropyl, or methacryloxypropyl groups. The carbofunctional polysiloxanes may also be terminated with alkene groups (e.g. allyl groups) or with arylamine end groups: $-C_6H_4NH_2$ (Kawakami & Abe, 1992). Quite often for synthesis of the carbofunctional polydimethylsiloxanes are used α,ω-dihydrosiloxanes, which are synthesized in condensation reactions of polysiloxane-α,ω-diols with chloro(hydro)-dimethylsilane. The CFPS containing terminal carbinol groups (C-OH) are products of hydrosilylation reaction of different α,ω-dihydropolysiloxanes with allyl derivatives (Marciniec et al., 1992b), e.g. allyloxytrimethylsilane (Greber & Jäger, 1962), followed by hydrolysis reaction of alkoxysilane end groups (Scheme 1).



Scheme 1. The preparation of α,ω-di(hydroxypropyl)polydimethylsiloxanes.

The hydrosilylation is the fundamental reaction used for the preparation of the carbofunctional polysiloxanes (Brook, 2000; Marciniec et al., 1992b), and platinum Speier's and Karstedt's catalysts are not enough effective in the case of addition of allylamine to tetramethylcyclotetrasiloxane D_4^H (D^H = MeHSiO), giving low yield and selectivity of products (Wu & Feng, 2001). Instead of a very useful catalyst of this reaction is platinum oxide PtO_2, 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 to β 93:7 (Zhou et al., 2004).

A very common method of the preparation of the carbofunctional polysiloxanes are catalytic equilibration reactions of cyclic siloxanes, e.g. octamethylcyclotetrasiloxane $(Me_2SiO)_4$ (D_4) with carbofunctional disiloxanes, which are carried out in acidic or basic media (Scheme 2) (Yilgor & McGrath, 1988; Harabagiu et al., 1996).

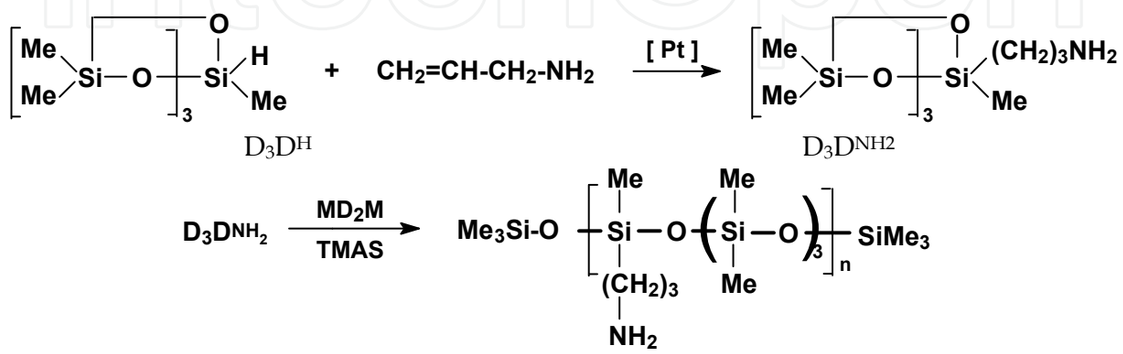


Scheme 2. The preparation of CFPS by the catalytic equilibration of the carbofunctional disiloxanes with D_4.

For example, by the equilibration of D_4 (D = Me_2SiO) with (3-aminopropyl)methyldiethoxysilane and hexamethyldisiloxane $Me_3SiOSiMe_3$, polydimethyl-*co*-[(aminopropyl)(methyl)]-siloxane oils (containing side aminopropyl groups) were prepared (Yang et al., 2007).

By anionic copolymerization of D_4 with $(Ph_4SiO)_4$ and $(ViMeSiO)_4$ towards 1,3-bis(3-aminopropyl)tetramethyldisiloxane (as a chain terminating agent) poly(dimethyl-*co*-diphenyl)-siloxane containing terminal aminopropyl groups was prepared. This product was utilized for a synthesis of a segmented poly(imide-siloxane) copolymer, and subsequently for the preparation of a hybrid nanocomposite, reinforced with silica (Liaw, 2007a) or titania TiO_2 (Liaw, 2007b).

The carbofunctional polysiloxanes, in which alkylfunctional groups are attached to the silicon atoms inside of the polymer chain were also prepared by the catalytic equilibration of cyclotetrasiloxane, containing aminopropyl functional groups (D_3D^{NH2}), with decamethyltetrasiloxane MD_2M (D = Me_2SiO, M = $Me_3SiO_{0.5}$) in the presence of $Me_4NOSiMe_3$ (TMAS) (Zhou et al., 2004; Yang et al., 2007), as it is presented on a Scheme 3:



Scheme 3. The preparation of CFPS with pendant aminopropyl functional groups.

By a controlled hydrolytic copolycondensation of (3-aminopropyl)(methyl)diethoxysilane and [(3-aminoethylamino)propyl](methyl)dimethoxysilane - a mixture of linear and cyclo-siloxane oligomers containing 3-aminopropyl and [(3-aminoethylamino)propyl substituents was prepared (Kichler et al., 2003). They were applied as new generation polycationic supports of DNA ("*gene transfer reagents*").

Carbofunctional PDMS with different photoactive linkages, i.e. benzoin (Yagci et al., 1994), glicydoxyl (Harabagiu et al., 1995), or benzylacryl groups (Iojoiu et al., 2000) were also prepared.

The synthetic methods, mentioned in this Chapter, do not cover many other methods of the preparation of the carbofunctional polysiloxanes.

2.5 Polyhedral Silsesquioxanes (POSS)

Silsesquioxanes (SSO) are important hybrid materials. Silsesquioxane or T unit of general formula $RSiO_{1.5}$ can exist in several structural types such as random, ladder, cage or semi-cage structures. SSO with a cage structure is also called polyhedral oligomeric silsesquioxane (POSS). POSS are organic-inorganic molecules, approximately 1-3 nm in size, with a general formula $(RSiO_{1.5})_n$ or T_n, where R is mostly organic group, which can be suitable for polymerization or grafting (Baney et al., 1995). Among various oligosilsesquioxanes, aromatic POSS are the most interesting compounds because of their high temperature stability (> 500 °C for octaphenylsilsesquioxane).

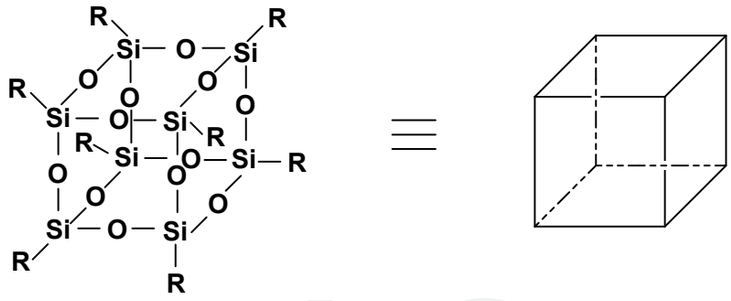


Fig. 2. Chemical structure of T_8 (Williams et al., 2011).

3. Technical applications of reactive silanes and siloxanes

An interest concerning the carbofunctional silanes is still growing and broadens a scale of their numerous applications. A great practical meaning have also carbofunctional polysiloxanes.

3.1 Applications of carbofunctional silanes

The carbofunctional silanes $X_nSi(R'Y)_{4-n}$ have found misceleneous practical applications thank to the presence of two kinds of the functional groups X and Y. In practice formation of chemical bonds with an inorganic material is possible, as a result of reactions of functional groups X, which most often are alkoxy groups. On the other hand the functional groups Y enable reactions with organic polymers. Most popular, available on market, are compounds of a structure $(RO)_3Si(CH_2)_3Y$, in which as alkoxy substituents are present methoxy or

ethoxy groups, and as organic functional groups Y: amine -NH_2, glicydyloxy -O-CH_2-(CH-CH_2O) or methacryloxy –O-CO-C(CH_3)=CH_2 groups.

3.1.1 Processes sol-gel

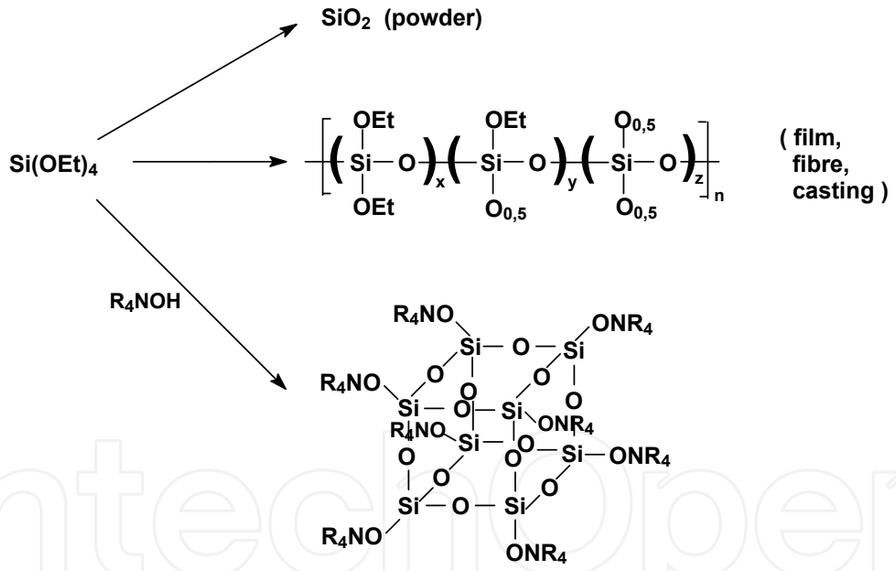
The carbofunctional silanes are often used in sol–gel processes for a preparation of hybrid organic–inorganic materials (Brinker, 1990; Schmidt, 1984, 1994). In sol–gel systems take place hydrolysis and condensation reactions of alkoxysilanes, described by equilibrium elementary reactions (4)-(6), which are catalyzed both by acids and bases:

$$\equiv\text{Si-OR} + H_2O \Leftrightarrow \equiv\text{Si-OH} + \text{ROH} \quad (4)$$

$$\equiv\text{Si-OR} + \text{HO-Si}\equiv \Leftrightarrow \equiv\text{Si-O-Si}\equiv + \text{ROH} \quad (5)$$

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \Leftrightarrow \equiv\text{Si-O-Si}\equiv + H_2O \quad (6)$$

In an acidic medium hydrolysis reactions undergo faster than condensation reactions, but in a basic medium condensation reactions are faster. Products of the sol–gel process of tetraethoxysilane are: silicagel, branched poly(ethoxysilicates) or silsesquioxanes, as it is presented on a Scheme 4 (Abe & Gunji, 2004).



Scheme 4. Products formed in the sol–gel process of tetraethoxysilane.

New 2,6-di-tert-butylphenol antioxidants and their derivatives containing trialkoxysilane linkages were prepared by the sol-gel method. They were applied for a stabilization of isotactic polypropylene (Nedelcev et al., 2007). The sol–gel technique is also applied in order to get organic materials with better properties, through an introduction of metal alkoxides.

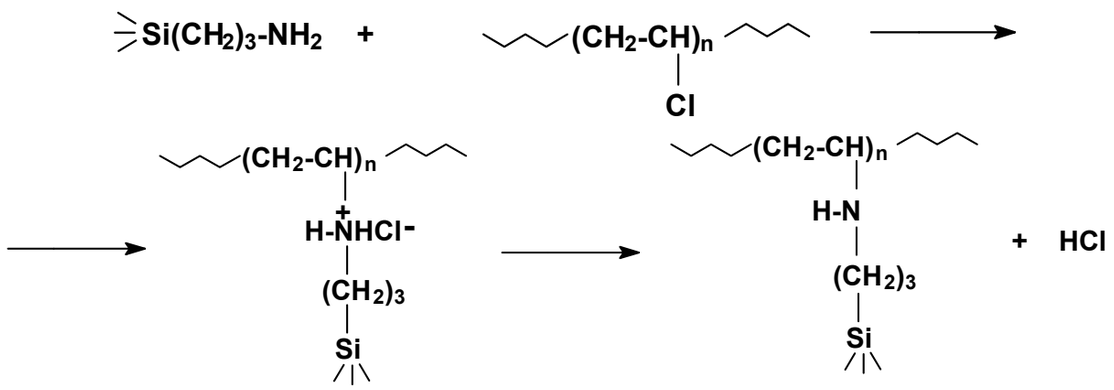
3.1.2 Modification of polymers properties by CFS

The carbofunctional silanes have found wide applications in modifications of many organic polymers. For example, unsaturated polyesters modified with (methacryloxypropyl)silanes

are utilized in a manufacture of glass-reinforced laminates. Silanes containing oxirane groups are applied for surface treatment of fillers which are used in epoxide composites. They are also utilized for the modification of novolac resins through reaction of hydroxyl groups of phenol with epoxy groups. Polycarbonates (PC) and polysulphones (PSU) form amide or sulphonamide bonds, and polyurethanes – urea bonds, respectively. This way modified polyamides, PC and PSU can be easier reinforced with the fillers, giving composite materials showing very good mechanical properties (Arkles, 1977).

For the modification of polymers most often are used (aminoalkyl)silanes. Chlorinated polymers, e.g. poly(vinyl chloride) (PVC), easily form quaternary salts with (aminoalkyl)-silanes (Scheme 5).

Silane agents, terminating polymer chains (”*endcappers*”), were prepared by addition Michael reactions of (3-aminopropyl)trimethoxysilane to acrylates. They were used for an introduction of trimethoxysilane groups on chain ends of polyurethanes, enabling their cross-linking under action of atmospheric moisture. It established a base for elaboration of a technology of newer one-component, solventless adhesion materials (”*solvent-free*”) (Nomura et al., 2007).



Scheme 5. Reactions of (aminopropyl)silane with PVC.

The carbofunctional silanes are also applied for the surface modification of the inactive fillers and polymers, e.g. in polyolefin composites filled with calcium carbonate or mica (Han et al., 1981; Okuno & Woodhams, 1975; Scott et al.; 1987; Trotignon et al., 1986). Polypropylene filled with $CaCO_3$ is the fundamental plastic, from which are produced garden furniture. Two aminofunctional silanes were applied for improvement of a tensile strength and decrease of deformability of the polypropylene composites containing non-modified $CaCO_3$ and modified with silanes (Demjen et al., 1997, 1998, 1999; Pukanszky, 2005). The polycondensation of triethoxysilyl groups under process conditions takes place quickly as well and leads to a reinforcement of interactions between ingredients of the composite PP/$CaCO_3$ (Demjen et al., 1997).

3.1.3 Modification of polyolefins

Polyolefins are the most widely used group of commodity thermoplastics. A cross-linking is one of modification methods of polyolefins (PO) properties, such as high temperature

stability, chemical and stress cracking resistance, and also as shape memory. It can be done by different methods: irradiation, peroxide process, azo process, and moisture curing of silane-functionalized polyolefins (Munteanu, 1997; Morshedian & Hoseinpour, 2009). The last technique (SIOPLAS technology) was developed in the late 1960s, and modified in the late 1980s. Both irradiation and peroxide cross-linking processes have some disadvantages such as high costs for irradiation equipment, the possibility of pre-curing in peroxide cross-linking processes, the inability to crosslink PP through tertiary-bonded carbon atoms and the formation of voids in cable insulations.

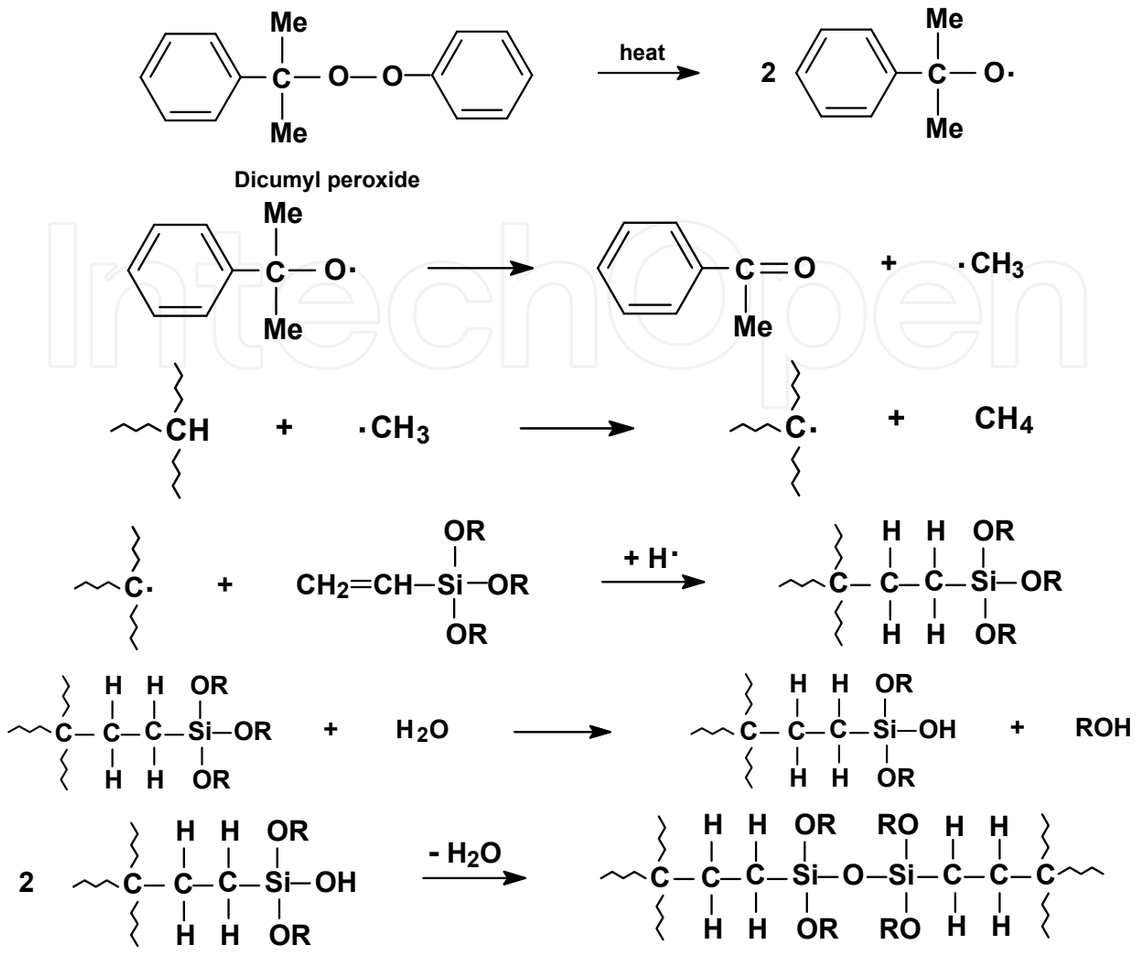
3.1.3.1 Silane-crosslinked polyolefins

The new cross-linking SIOPLAS technology, patented by Dow Corning, is a two-step process, based on the chemistry of organofunctional silanes, which are first grafted on polyolefins chains. In a second post-reactor step the siloxane cross-linkages (Si-O-Si) are formed. Alkoxysilanes, most often vinyltrimethoxysilane (VTMS), are melt grafted on polyolefins in processing equipment, usually extruders, in the presence of small amounts of peroxides as radical initiators. Vinyltriethoxysilane (VTES), and especially 3-methacryloxypropylsilane have limited application. Usually, about 2 % of silanes are used, and dicumyl peroxide as the initiator is used (5-15 wt. %). The silane grafting reaction is very fast and it allows the choice of reactive processing to be the industrial synthetic method. Within a few minutes of the residence time of all components in the extruder, very high grafting yields are obtained (at least 80 % of the added silane is grafted onto PE) in an optimized industrial process. The possibility of silane homopolymerization may be almost excluded under the conditions of reactive processing. The reactive processing techniques enable silane grafting onto any kind of olefin homopolymer (LDPE, linear LLDPE, HDPE, very low density VLDPE, PE waxes, all kinds of PP), PO blends or copolymers (EVA, EP and EPDM elastomers), and polyisobutene (Munteanu, 1997).

The silane-grafted POs are still thermoplastic cross-linkable products, which are processed in the usual way in finished goods subsequently subjected to cross-linking in the presence of moisture. The alkoxysilyl groups hydrolyse to form silanol groups Si-OH, which condense to generate the siloxane bonds responsible for the formation of the three dimensional network. Before the moisture cross-linking step a master batch containing 0.05-0.15 wt. % (and even 2.0-3.6 wt. %) of an organotin catalyst is melt mix with the silane-grafted PO in order to achieve cross-linking rates of practical importance. Cross-linking takes place beside the production line in hot water tanks or steam chambers, most often at 60-90 °C. Under these conditions the curing time is in a range from a few hours or days.

The silane cross-linking has many advantages among curing technologies. Most of those advantages are the consequence of separating the cross-linking step from the shaping step and the specific structure of the network as well, the latter feature is responsible for better thermomechanical properties in comparison with peroxide cross-linked networks.

A modified one-step version of this technology, called as MONOSIL process, appeared few years later. All the components, i.e. polyethylene + silane + grafting initiator + cross-linking catalyst, were added in a high-shear mixing extruder wit a longer screw (Thomas & Bowrey, 1977; Swarbrick et al., 1974).



Scheme 6. Basic reactions involved in silane grafting onto PE and further cross-linking of PE (Morshedian & Hoseinpour, 2009).

An alternative method to the silane grafting is a one-step random copolymerization of ethylene with vinyltrialkoxysilanes at high pressure (150-350 MPa) and temperature (180-290 °C) in the presence of free radical initiators (usually peroxides), which was developed by Union Carbide and Mitsubishi Petrochemicals. This process has some advantages, since the silane units (< 5 wt. %) can be randomly and homogeneously distributed in the polymer chain, so it was possible to achieve a certain degree of cross-linking with a small amount of the silane incorporated in the polymer. There is also no limitation in the choice of antioxidants as in the case of peroxide and silane grafting cross-linking process (Eagles, 1990; Munteanu, 1997).

A copolymer of ethylene with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, a poly(ethylene-*co*-divinylsiloxane), was synthesized in a high pressure reactors at 180-220 °C and p ≈ 1300 bar (Smedberg et al., 2004).

3.1.3.2 Hydrosilylation of polyolefins

A hydrosilylation of terminal double bonds in polyolefins through reactive processing is a next important modification method of these thermoplastics:

$$\equiv Si\text{-}CH{=}CH_2 \; + \; H\text{-}Si\equiv \longrightarrow \equiv Si\text{-}CH_2\text{-}CH_2\text{-}Si\equiv$$

Polypropylene containing terminal double bonds was modified with a hydride-terminated polydimethylsiloxane (PDMS) at three different temperatures through a hydrosilylation reaction, catalyzed by Karstedt's platinum catalyst in the melt phase (Malz & Tzoganakis, 1998; Long et al., 2003, 2004). The double bonds were formed by peroxide initiated degradation of PP in an extruder or a batch mixer. An organic peroxide, Lupersol 101, was used in concentrations of 0.5-5 wt. %. A hydride-terminated polydimethylsiloxane was used as a substrate hydrosilylating the terminal double bonds of the degraded polypropylene (DPP). Reactive processing experiments were carried out in a hot press, a batch mixer, and a single screw extruder. The reaction time of the hydrosilylation reaction was short enough to be completed in a screw extruder. This made possible the simultaneous extrusion and modification of polypropylene.

Two different reaction mechanisms were used to initiate the hydrosilylation reaction: a radical chain addition mechanism and a platinum catalyzed mechanism using platinum Karstedt's catalyst. It was found that both reactions, degradation and hydrosilylation, could be performed simultaneously, by using high peroxide concentrations, while previously degraded polypropylene could be hydrosilylated with catalytic amounts of a peroxide. For the catalytic mechanism, the required stabilization of the platinum colloid formed in this mechanism was accomplished by adding *t*-butylhydroperoxide as a co-catalyst.

The hydrosilylation of polybutadiene (PB) with hydrosilanes is catalyzed by rhodium and platinum catalysts, and platinum-nanoclusters and it is a source of silyl derivatives of PB, many of them have functional group and can find useful applications (Guo et al., 1990; Iraqi et al., 1992; Chauhan & Balagam, 2006; Chauhan et al., 2008).

A comprehensive study on the surface characteristics of hydrosilylated polypropylene was conducted by combining macroscopic thermodynamics, microstructure, and chemical composition measurements (Long et al., 2003, 2004). A positive effect of a poly(dimethyl-siloxane) modified polyolefin additive on the processing and surface properties of linear low density polyethylene (LLDPE) was observed (Zhu et al., 2007). A polydimethylsiloxane (PDMS) modified polyolefin, obtained by reacting an ethylene-ethyl acrylate-maleic anhydride (EEAMA) copolymer with an amine terminated PDMS in the melt phase, was used as a processing aid to facilitate the extrusion of LLDPE. Surface properties of hydro-silylated polyolefins could be further modified by annealing in supercritical carbon dioxide (Zhu & Tzoganakis, 2008). Two hydrosilylated polypropylenes (PP) and polyethylenes (PE) were obtained by reacting with di- and multi-functional hydride terminated poly(dimethyl-siloxane). Processing properties of polypropylene were improved by the addition of a small amount (~2 wt. %) of silicone oil (Zhang et al., 2010).

A PDMS grafted copolymer, which can be potentially applied as a processing agent or a surface property modifier, was synthesized via reactive melt mixing of ethylene–ethyl acrylate–maleic anhydride terpolymer (EEAMA) and aminopropyl terminated PDMS (McManus et al., 2006).

Crosslinked styrene-isoprene-siloxane copolymers were applied for a preparation of membranes useful for pervaporative removal of volatile organic compounds from water.

The membranes were prepared from the crosslinked copolymer composed of elastomeric glassy styrene-isoprene prepolymer and oligo- or polyhydrosiloxanes (Kerres & Strathmann, 1993; Kujawski et al., 2003). The pervaporation properties of the membranes, used for pervaporation of water–methyl acetate and water–methyl *tert*-butyl ether mixtures, depend on the siloxane content in the membrane and were much better than properties of the commercially available hydrophobic membranes.

High molar mass copolymers of ethylene or propylene with α-olefin macromonomer, monovinyl-functional silsesquioxane cage 1-(9-decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo-[9.5.1.13,9.15,15.17,13]octasiloxane, were obtained in the presence of metallocene catalysts, activated with alumoxanes. These copolymers, contained up to 25 wt. % (1.2 mol. %) of spherosilicate pendant units, which accounted for a decrease of the melting temperature by 18 K with respect to PE. A thermostability under air was improved in the polyethylene copolymer in comparison to PE (Tsuchida et al., 1997).

3.2 Applications of carbofunctional polysiloxanes

The carbofunctional polysiloxanes are most often used for syntheses of hybrid silicone-organic copolymers and for the modification of many polymers and plastics. This way, numerous new polymeric materials with profitable properties were obtained.

3.2.1 Modification of vinyl and acryl polymers by CFPS

The graft copolymers of polysiloxane with styrene, methyl metacrylate, and chloroprene were synthesized by a radical polymerization from the commercial carbofunctional polysiloxanes containing side and terminal mercaptopropyl groups (Fawcett et al., 2001).

3.2.1.1 Polystyrene

Block copolymers comprised of chemically distinct polymers covalently joined together self-organize in bulk into well-defined nanoscopic structures including lamellar, cylindrical, and spherical morphologies. There are a lot of block copolymers based on styrene monomers with reactive alkoxysilyl groups. A series of well-defined poly(3-methacryloxypropyltriethoxysilane)-*b*–polystyrene (PMAPTES-*b*-PS) diblock copolymers was prepared via sequential RAFT polymerization (Zhang et al., 2007). Poly(acryloxypropyltriethoxysilane)-*b*-polystyrene (PATPES-*b*-PS) diblock copolymers were prepared by the nitroxide-mediated polymerization (NMP) using alkoxyamine initiators (Gamys et al. 2010). The core-shell particles prepared by emulsion polymerization of styrene and subsequent addition of MPTMS have been used to produce hybrid nanocapsules (Ni et al., 2008). A series of well-defined rod-coil block copolymers poly(dimethylsiloxane-*b*-poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene} (PDMS-*b*-PMPCS) containing a CO_2-philic block PDMS was synthesized through ATRP (Shi et al., 2011). The nanostructure of these copolymers changed from lamellae (LAM) to hexagonally packed cylinders (HEX) according to the volume fraction of PDMS in block copolymers. The microemulsion photocopolymerization of styrene and butyl acrylate in the presence of silane coupling agent, such as MAPTMS, using 2-hydroxy-2-methylpropiophenone as photoinitiator was carried out as well (Wan et al., 2009). The copolymer particles were nearly spherical and were very uniform with the number average particle size of 25.5 nm and M_w/M_n of 1.11.

Particles with structural and compositional anisotropy are great interest for potential applications such as optical switches and filters. Anisotropic particles are composed of various materials such as functional polymers and inorganic materials with a high refractive index. Nagao et al. (2008) demonstrated monodisperse, anisotropic particles composed of organic and inorganic materials, prepared in a two step soap-free emulsion polymerization. In the first step, seed polymer particles were prepared in the presence of MPTMS in water. In the second step, another polymerization of styrene and/or methyl methacrylate was conducted in the presence of seed particles, which induced anisotropic protrusion of polymer from the seed particles. This method is applicable to the preparation of anisotropic polymer particles containing inorganic particles such as silica.

The transparent hybrid materials were obtained by a bulk polymerization with styrene, ethylene glycol dimethacrylate (EGDMA), and silicone macromonomer containing PDMS chains with urethane and methacrylate functionalities (SiUMA) (Daimatsu et al., 2008). The prepared P(S-*co*-SiUMA-*co*-EDGMA) copolymers were transparent, similarly to pure PS, while P(S-*co*-SiUMA) copolymers were opaque.

The simple method for preparing block copolymers of PDMS and vinyl monomers was reported (Oz & Akar, 2006). PDMS-*b*-PAN and PDMS-*b*-PS copolymers were produced in one step with redox system of α,ω-dihydroxypropyl terminated PDMS/ceric ammonium nitrate at ambient temperature in water. The copolymer products had much higher contact angle values than corresponding homopolymers, although their silicone content was as low as 1-2 wt. %. These copolymers may act as compatibilizers in the blending application of vinyl polymers with polysiloxanes.

3.2.1.2 PVAL

Silicone polyoxyalkylene copolymers are the most known silicone surfactants because of their biodegradability, biotolerance and water solubility, e.g. poly(vinyl alcohol)-*graft*-PDMS (Pouget et al., 2008). These copolymers have been synthesized in aqueous dispersion of a mono- or diepoxy terminated PDMS with pendant alcohols of P(VAL-*co*-VAC). The last copolymer was used as a dispersant to stabilize the PDMS microsuspension and the reaction took place at the interface of the silicone droplets. The preparation of PVAL-PDMS copolymers is of great interest, especially for the preparation of PVAL-PDMS amphiphilic copolymers. The incorporation of PDMS block in the PVAL structure would enhance its flexibility and resistance to moisture. Lacroix-Desmazes et al. (2008) reported synthesis of triblock copolymer PVAL-*b*-PDMS-*b*-PVAL.

3.2.1.3 PVDF

Poly(vinylidene fluoride) (PVDF), semicrystal membrane materials, were recently obtained. They showed high strength and good chemical resistance. However their relative hydrophobicity and inactivity have limited their use in materials for membrane separation of oil and biological molecules. For these applications the increase of PVDF hydrophilicity was necessary. PVDF as a macroinitiator was grafted with 3-methacrylate propyltrimethoxysilane (MAPTMS) via ATRP of MAPTMS. The flux of the membrane prepared from silylfuctionalized PVDF was much higher than that of the membrane prepared from parent material (Chen & Kim, 2008). Another limitations in application of PVDF are its poor solubility and difficulty in cross-linking. Low-molecular-weight copolymers obtained by

copolymerization of fluorinated monomers bearing an ω-trialkoxysilane function with vinylidene fluoride (VDF), were successfully cross-linked in the presence of moisture and these cross-linked materials showed interesting repellent properties with respect to boiling acetone, water, acids, and oil (Guiot et al., 2006).

3.2.1.4 Acryl polymers

Some silyl derivatives of polymers such as acrylates, methacrylates show membrane properties with the selectivity with reference to oxygen. Thus silyl methacrylate may be used in contact lenses. The synthesis of 2-hydroxyethyl methacrylate (HEMA) polymers modified with some silyl groups was carried out. The increase of polymethacrylates solubilities with increase of incorporation of silyl groups was observed (Assadi et al., 2005).

Polymerization strategies to overcome limiting monomer conversion in silicone-acrylic miniemulsion polymerization were presented (Rodriguez et al., 2008). The waterborne silicone-modified acrylic materials were obtained from divinyl terminated PDMS and methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA).

Thermoresponsive shape memory polymers (SMPs) are the most studied materials because of their potential applications in biomedical fields. Poly(N-isopropylacrylamide) (PNIPAAm) is a typical example that exhibits a lower critical solution temperature (LCST) at ca. 32 °C in water solution. Below this temperature PNIPAAm chains are soluble due to the hydrogen bonding interactions between polymer chains and water molecules, whereas the phase separation occurs and the polymers precipitate from the solution when the temperature is above the LCST. A series of monodisperse microgel with different particle sizes and cross-linking density were prepared by precipitation copolymerization of NIPAAm with 3-methacryloxypropyltriethoxysilane (MAPTES). The experimental results revealed that the microgel exhibited temperature sensitivity and the phase transition temperature approximately at 31 °C. A decrease of MAPTES content resulted in a reduction of the final hydrodynamic diameters of the microgel (Zhang et al., 2009).

A self-assembly silane monolayer was formed by 3-aminopropyltriethoxysilane (APTES), followed by the graft polymerization of NIPAAm on the glass surface. These kind of glasses bonded with NIPAAm films have potential applications as environmentally switchable materials (Wang et al., 2005).

PDMS have been widely used in a variety of biomedical applications, but their hydrophobicity is often a problem. This can be overcome with the introduction of hydrophilic polymers, such as poly(N,N-dimethylacrylamide) (PDMAAm). The synthesis of a new family of amphiphilic multiblock and triblock copolymers (PDMAAm-*b*-PDMS-b-PDMAAm) via RAFT polymerization was proposed (Pavlovic et al., 2008). A novel ABC triblock copolymer with very low surface energy: PDMS-*b*-PMMA-*b*-PHFBMA (2,2,3,3,4,4,4-heptafluorobutyl methacrylate) was successfully synthesized via ATRP by Luo et al. (2008). The lowest surface energy of these triblock copolymers reached 3.03 mN/m, thus the PDMS-*b*-PMMA-*b*-PHFBMA could be applied as an antifouling coating.

A next interesting application of the CFPS is their utilization in synthesis of interpenetrating polymer networks (IPN) with fluorinated acrylates. These siloxane-fluoroacryl IPN networks were prepared *in situ* from of α,ω-(3-hydroxypropyl)polydimethylsiloxanes,

isocyanurate derivatives of hexamethylene diisocyanates $R(NCO)_x$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol, ethylene glycol dimethacrylate (EGDMA), dicyclohexyl acrylate, and dipercarbonate (DCPD), towards dibutyltin dilaurate (DBTDL). A transparency of the obtained materials gave an evidence that no phase separation took place. The fluorinated polymers exhibit good hydro- and oleofobicity (Darras et al., 2007).

3.2.1.5 Radical polymerization of dissymmetric fumarates

Polymerization of fumarate monomers provide polymers with a substituent in every methylene unit. These polymers are applied as high performance materials, as bio-degradable polymers, low dielectric materials, oxygen permeability membranes, liquid crystal, contact lens (CL) materials, etc. Among them, CL is known well as the lens equipped on a cornea foe vision correction, and the CL materials are required both for the oxygen permeable property for breathing of corneal cell and the hydrophilic property for not repelling a tear and to protect a lipid deposition. Polymerizations of amphiphilic fumarate (containing hydrophilic and hydrophobic substituents) monomers give polymers with high oxygen permeability, hydrophilicity and transparency required for CL materials. Novel dissymmetric fumarate monomers having both alkoxyethyl group [2-(2-methoxyethoxy)-ethyl, 2-(2-(2-methoxy-ethoxy)ethoxy)ethyl] and a bulky 3-[tris(trimethylsiloxy)silyl]propyl group were radically polymerized with styrene and N-vinylpyrrolidone (NVP). Various membranes, prepared by copolymerization of fumarate monomers with NVP or NVP and HEMA, showed much better transparency, as compared to the membranes containing 3-[tris-(trimethylsilyloxy)silyl]propyl methacrylate (Ohnishi et al. 2009).

3.2.2 Modification of condensation thermoplastics by CFPS

3.2.2.1 Polyesters

Enzymatic polymerization is an environmentally friendly approach to polymer synthesis and in the contrast to traditional chemical methods it does not need harsh reaction conditions and metallic catalysts. Lipase-catalyzed synthesis of aromatic silicone polyesters (SAPEs) and polyamides (SAPAs) have been reported (Poojari & Clarson, 2010). The SAPEs were synthesized using α,ω-dihydroxyalkyl-terminated PDMS, and the SAPAs were prepared with α,ω-diaminoalkyl-terminated PDMS via transesterification reaction with dimethyl terephthalate in toluene at a temperature in the range 80–90 °C. Both types of polymer were liquids at room temperature. Polysiloxane-polyester copolymers were synthesized by polycondensation of a series of diacids and α,ω-bis(3-hydroxypropyl)-PDMS with Novozyme-435. The use of lipase as the catalyst led to carry out the polycondensation reaction under mild conditions (Guo et al., 2008).

A series of novel thermoplastic elastomers, poly(ester-siloxane)s, have been synthesized (Antic et al., 2010). These materials were based on poly(butylenes terephthalate) (PBT) as the hard segments and PDMS-containing prepolymers as the soft segments. In order to increase the compatibility of PDMS copolymers of siloxanes with terminal aliphatic polyester such a triblock copolymer polycaprolactone-*block*-polydimethylsiloxane-*block*-polycaprolactone (PCL-*b*-PDMS-*b*-PCL) was used. The thermal stability of the poly(ester-siloxane)s was higher than that of PBT homopolymer, and the reduced crystallinity of the hard segments have been observed.

Thermoresponsive shape memory polymers (SMPs) are a class of materials that change shape upon exposure to heat. They are lightweight, easy to fabricate and may be biodegradable. Poly(ε-caprolactone) (PCL)-based SMPs have received much attention due to the biocompatibility, biodegrability, and elasticity of PCL. PCL is useful as a crystalline switching segment for SMPs as its T_{trans} is a well-defined T_m in the range of 45-60 °C with increasing M_n. Such T_{trans} values are useful for *in vivo* deployment as well as other applications which require low heating. To modify properties of PCL-based SMPs, AB polymer networks have been prepared through incorporation of organic hard or soft segments. PDMS with extremely low T_g (-123 °C) is a particularly effective soft segment candidate. Schoener et al. (2010) prepared organic-inorganic SMPs comprised of inorganic PDMS segments, terminated by aminopropyl groups, and organic PCL segments. The resulting SMP network exhibited excellent shape fixity and recovery. By changing the PDMS length, the thermal, mechanical, and surface properties were systematically alternated.

Carbon nanotubes (CNTs) are the ideal reinforcing agents for high-strength polymer composites because of their tremendous mechanical strength, their Young's modulus is ca. 1000 GPa and it is much higher than that of the conventional carbon fibres (200-800 GPa). For good reinforcement effect the surface of CNTs must be strongly bonded to the polymer matrix. Sidewall functionalization of CNTs, introduction mainly carboxylic groups, makes possible to chemically attach these nanofillers with polymers. Chen and Shimizu (2008) prepared the nanocomposites of poly(L-lactide) (PLLA) reinforced by aminopropylisooctyl POSS modified multi-wall nanotubes (MWNTs) (MWNT-*g*-POSS). They have observed the homogeneous dispersion of MWNTs throughout the PLLA MWNT-*g*-POSS composites without any aggregation. The fractial surface of the composites showed not only a uniform dispersion of MWNTs but also a strong interfacial adhesion with the matrix.

3.2.2.2 Polyamides

Alongi et al. (2009) have reported the preparation of inorganic-organic hybrids made of POSS and polyamide 6 (PA 6) produced by melt mixing of the two components or by the *in situ* polymerization of ε-caprolactam in the presence of POSS. The last method did not result in any POSS self-aggregation in the polymer matrix, achieving a very fine cubic dispersion of nanometric dimensions. The nearly nano-sized aromatic polyamide particles with amino groups, known as poly(amino-amide) PAMAM, were prepared by Yoshioka (2009). They were modified with silane coupling agent, i.e. 3-glycidoxypropyltriethoxysilane (GPTES), and further complexed with ZnO particles. The finally ZnO-based materials have specific optical properties: they show excellent optical absorption properties in UV region and high transmittance in the visible region.

3.2.2.3 Polyimides

Polyimides (PIs) are well-known engineering plastics with excellent thermal, mechanical, dielectric, and optical properties. They also have good chemical resistance and high dimensional stability. However the main deficiency of aromatic polyimides is their insolubility in organic solvents and infusibility or extremely high glass transition temperature (T_g) which makes their processing very difficult. One approach to increase the solubility and processability of polyimides is the introduction of flexible linkages or bulky units into the polymer chain. The incorporation of PDMS sequences in PIs has afforded new copolymers with good processability, low water absorption, atomic oxygen resistance, and excellent

adhesion. The unique properties of the imide-siloxane copolymeric materials (PSIs) make them especially attractive for applications in microelectronics and as structural adhesives.

A series of amorphous poly(imide siloxane)s (PIS) with different PDMS contents and segmental lengths were synthesized via condensation reaction by Ku & Lee (2007). A variety of morphologies of PIS films, including unilamellar vesicle, multilamellar vesicle, sea-island and others, were found as the function of the content and the segmental length of PDMS, as well as the coexistence of large-scale phase separations and nano-scale phase separation of approximately 20 nm.

Lu et al. (2006) prepared, using sol-gel method, polyimide/polydiphenylsiloxane (PI/PDPS) composite films with high thermal stability near pure PI. Polysiloxanes well dispersed in polyimide matrix, without macroscopic separation for the composite films was observed with low content of DPS, while large domain of polysiloxane was formed in films with high DPS content. The introduction of DPS into PI improved the elongation at break but the composite films still remained with higher modulus and tensile strength.

Aromatic polyimides (PIs) have been of great interest in gas separation membranes because of their gas selectivity and excellent thermal and mechanical properties. Recently, novel triamine-based hyperbranched PIs are applied for high-performance gas-separation materials. Hybridization of PIs with inorganic compounds has been focused also to improve the gas transport properties. Hyperbranched PIs prepared by polycondensation of a triamine 1,3,5-tris-(4-aminophenoxy)benzene and 4,4'-(heksafluoroisopropylidene) diphthalic dianhydryde (6FDA) were modified by sol-gel reaction using tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS), and 3-aminopropyltrimethoxysilane (Suzuki et al., 2008).

New copolymers, polysiloxane-imides (PSIs), have been prepared from α,ω-(bisamino-propyl)dimethylsiloxane oligomers (ODMS) and aromatic dianhydrides: 1,2,4,5-benzene-tetracarboxylic dianhydride (PMDA), and 6FDA, (Krea et al., 2004). Membranes of these new PSIs have been used to remove polar organics from water by pervaporation.

Bismaleimide (BMI) has the unique combination of a high service temperature, good toughness and epoxy-like processing. Composites of BMI with surface-modified SiO_2 nanoparticles by amino-functionalized silane coupling agent has been studied (Yan et al., 2008). The nanocomposites with surface-modified SiO_2 showed better wear resistance and lower frictional coefficient than that with unmodified fillers.

3.2.2.4 Modification of polycarbonates by CFPS

Polycarbonates (PCs) belong to an extremely useful class of engineering thermoplastics known for their toughness and optical properties. Most commercialized PCs are based on bisphenol A and these polyesters have the advantageous properties of superior heat resistance, transparency, dimensional stability and self-extinction, exceptional impact resistance and ductility at or below room temperature. Other properties such as the modulus, dielectric strength and tensile strength, are comparable to those of other amorphous thermoplastics. The main limitations of PCs are their poor scratch, ultraviolet (UV), and solvent resistance, and their sharply decreased impact strength at low temperature.

PC/silicone oil blends, based on two kind of silicone oils: PDMS and polydimethyldiphenyl-siloxane PDMDPS, have been studied (Kim & Kim, 2008). A transition from brittle to ductile

failure was observed with increasing PDMDPS content. At temperature of –30 °C the impact strength increased from 8 kg_fcm/cm to 52 kg_fcm/cm for neat PC and PC/PDMDPS blends respectively.

An interesting group of thermoplastic elastomers (TPE), characterized by a great stiffness at low temperature, are block copolymers prepared from polycarbonates (PC) and PDMS (PC/PDMS). Copolymers PC/PDMS are usually prepared in reaction of phosgene with bisphenol A in the presence of PDMS containing terminal bisphenol groups (van Aert et al., 2001). Block PC/PDMS copolymers find applications in a manufacture of membranes, which are used for selective separation of gases (LeGrand, 1972).

Multi-walled carbon nanotubes/polycarbonate nanocomposites (MWNT/PC) have been prepared (Wang et al., 2010). Functionalized MWNTs-COOH with α,ω-3-aminopropyl-PDMS, were used to produce MWNT/PC nanocomposites. The results showed that siloxane–modified carbon nanotubes were dispersed well in the PC matrix, and the tensile strength, flexural strength, flexural modulus, and flame retardancy of MWNT/PC composites were better than these of MWNT-COOH/PC. Siloxane-modified MWNTs can improve the electrical properties of the nanocomposites at low loading in PC.

3.2.3 Modification of polyurethanes and polyureas by CFPS

Thermoplastic polyurethanes (TPUs) are obtained by a polyaddition reaction of diisocyanates to long, hydroxyl-terminated oligomers (polyols) and short diols, which are often named as chain extenders. The polyurethanes are multi-block copolymers consisting of hard segments (HS) and soft segments (SS). The thermodynamic incompatibility between alternating segments usually induces a two-phase structure with soft domains containing mostly the polyol moieties, and hard domains made up of diisocyanate-chain extender sequences. If incompatibility exists between the two block components, a microphase separation will occur and the hard domains will provide a reinforcement to the system. The type of diisocyanate has a marked effect on a strength of a final material. The most often applied isocyanates are: 4,4'-methylenediphenyl diisocyanate (MDI), tolylene diisocyanate (TDI), bis(4-isocyanatocyclohexyl) methane (HMDI), isophorone diisocyanate (IPDI). TPUs are widely used for high-performance applications, as: medical implants (Arkles, 1983), membranes, adhesives and coatings, especially when a high tear and a tensile strength or good wear and abrasion resistance are required. Another special features of TPUs are their low-temperature elasticity, a smoothness for the touch, an electrical insulation and a good chemical resistance.

Over the past three decades, considerable attention has been directed to utilization of the PDMS as a soft segment component in polyurethanes and polyurethaneureas. Polysiloxane SS are introduced by PDMS-diols or hydroxyalkenyl or aminopropyl or ethyl-piperazine terminated PDMS. However, the tensile strength and elongation at break of these materials compared to those based on polyether (PET) or polyester (PES) SS are visibly poorer. Thus, various co-SS components, mainly based on poly(alkenyl oxide) have been utilized. Sheth et al. (2005) selected poly(propylene oxide) (PPO) as a second SS component, because his solubility parameter (23.5 $J^{1/2}/cm^{3/2}$) is in between that of PDMS (15.6 $J^{1/2}/cm^{3/2}$) and urea (45.6 $J^{1/2}/cm^{3/2}$). The inter-segmental mixing between PPO and urea segments could modify the nature of interphase between the soft matrix and the hard urea microdomains.

In order to reduce emission of volatile organic compounds, water borne polyurethanes (WPUs) have attracted much attention. However, the WPUs have shortcomings, such as lack of resistance to water, a surface hydrophilicity and the low strength. These disadvantages can be eliminated by using a different mixing composition of soft segments. Chen et al. (2005) prepared the anionic WPUs from hydroxyl-terminated PDMS, poly(tetramethylene oxide) (PTMO) as the soft segments, IPDI as the hard segment, and 2,2-bis(hydroxymethyl)-propionic acid (DMPA) as the ionic centre. DMPA was used to form a water-dispersible urethane prepolymer. The tensile strength of WPU-PDMS films decreased with an increasing content of PDMS and a water repellency reached 80 %, which was equal to a capability of the silicone rubber. These waterborne siloxane containing PUs are useful as textile coatings, leather finishing, sealants, plastic coatings, and a glass-fibre sizing.

A POSS-modified ionomeric polyurethane aqueous dispersion have been also reported for their improved reaction to fire and resistance to atomic oxygen as well as to the possibility to build nanostructured surfaces. As with other polymer systems, many of the POSS hybrids do yield elastomeric PU with improvements in physical and thermal properties at relatively low levels of POSS incorporation. The waterborne PU hybrid dispersions were synthesized by incorporating amino- and hydroxyl-terminated POSS macromers into the PU ionomeric backbones, using a homogeneous solution polymerization, followed by a solvent exchange with water (i.e., the "acetone process") (Nanda & Wicks 2006). The absence of crystalline domains evidenced the incorporation of POSS macromer in the PU hard segments.

Various researchers have shown that the gas permeability of PU membranes increases with the decrease of the hard segment content and the increase of the soft segment molecular weight. In addition, a correlation has been established between the gas permeability and the chemical nature of the polyols and chain extenders. Queirez & de Pinho (2005) investigated structural characteristics and gas permeation properties of PDMS-PPO-urethane/urea bi-soft segment membranes. The permeability of the membranes to CO_2, O_2 and N_2 increased with the increase of PDMS content. The $P(CO_2)/P(N_2)$ permeability ratio was higher for the bi-soft segment membranes in comparison with PDMS/PU membranes.

Some properties of PUs (high tear, tensile strength, good wear, abrasion resistance) are strongly jeopardized as soon as the service temperature of the material exceeds 70 to 80°C, mostly because of a creep phenomena. Dassin et al. (2002) tried to improve the working temperature of commercial TPU by creating a well-controlled chemical curing. The idea was to have an easily processible material with an improved thermomechanical behaviour. A commercial polyester-type TPU at first was reacted with a diisocyanate to create allophanate branching units, which at second step was grafted with 3-aminopropyltrimethoxysilane. Such materials could be crosslinked by a hydrolytic condensation mechanism, resulting in increased thermomechanical properties.

3.2.4 Modifications of other polymers and polymeric materials by CFPS

The CFPS were also used for synthesis of conductive siloxane-pyrrole block copolymers. An incorporation of flexible PDMS chains into the rigid polymer chain improves not only mechanical properties, but also solubility in different non-polar solvents. (N-pyrrole)-polysiloxane precursor, prepared in reaction of N-glicydylpyrrole with aminopropyl groups of PDMS was copolymerized with pyrrole (PY) by electrochemical methods, giving block

copolymer PY-PDMS. Classical conductive polymers are insoluble and infusible. A common way to facilitate their processing are syntheses of block or graft copolymers containing conductive segments and conventional segments, increasing solubility of copolymer, e.g. block copolymers of styrene and acetylene, styrene and thiophene, graft copolymers of pyrrole on polystyrene, and on poly(methyl methacrylate). Recently a new multifunctional polysiloxanes, containing mercapto-, thiocarbamide, and (hydroxyalkyl)ether linkages were applied for the modification of silica fillers used for the production of rubber tires (Kalaycioglu et al., 1998).

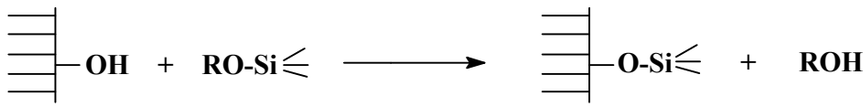
Copolymers with siloxane moieties serve as connectors with organic polymers (compatibilizers). Siloxane segments of the copolymers migrate to the surface, while organic segments act as anchors of siloxane blocks in the polymeric material.

3.3 Composites and nanocomposites from thermoplastic polymers

Composite materials consist of a polymer matrix and various inorganic fillers. They have been widely used in order to improve the mechanical, thermal, barrier, and other properties of the polymer. However it is known that the improvement of one property can result the worsening of another. It is anticipated that such problems can be overcome if the inorganic additive exists in the form of a fine dispersion within the polymer matrix producing a nano-composite. Silane modified fillers and nanofillers are used for these purposes.

3.3.1 Modification of fillers properties by CFS

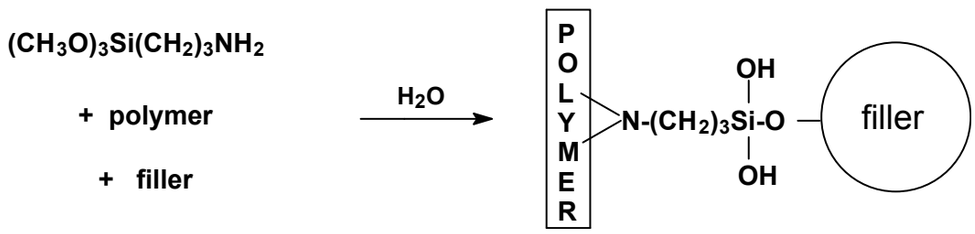
The carbofunctional silanes are most often applied as so called adhesion promoters, which are also called as "*silane coupling agents*" (Pleuddeman, 1991). The silane adhesion promoters are directly added to polymer compositions (usually in a quantity 0.2–2 % wt. %) or in a form of water and water-alcoholic dispersions. The substituent X (e.g. alkoxy group) may undergo condensation reactions with hydroxyl groups of the filler:



or hydrolysis reactions:



Thus alkoxy groups are replaced with silanol groups Si-OH, which are able to form chemical bonds with inorganic materials, e.g. glass, metals or fillers (Scheme 7) (Haas & Wolter, 1999):



Scheme 7. An adhesion model in a system: polymer–silane–filler.

The silanol functional groups Si-OH also undergo homocondensation reactions, with a formation of thermodynamically more stable siloxane systems Si–O–Si. Alternatively, Si-OH groups may react with OH groups of a surface of the filler. This way on the surface of the filler a layer of crosslinked polysiloxane is formed. An universality of an application of the fillers in plastics results from necessity of an improvement of mechanical, thermal, electrical, and magnetic properties of the polymers. The most often used fillers are: silica, calcium carbonate, calcium sulfate (gypsum), barium sulfate, calcium, aluminum (kaolin), and magnesium (talc and sepiolite) silicates, aluminum oxide and hydroxide, metal oxides (e.g. ZnO, MgO, CaO, TiO_2, Fe_2O_3, Pb_3O_4). An addition of nanofillers of particie size 10–50 nm profitably affects an increase of abrasion resistance of transparent polymer coatings and enables preparation of homogeneous composite of nanoparticles in a polymer matrix. The addition of 20–40 wt. % of the silica and alumina can improve abrasion resistance of material. The non-modified silicon and aluminum oxides have a large number of hydroxyl groups on the surface and thus they are hydrophilic materials. In the presence of non-polar liquids, e.g. acrylates, an aggregation of nanoparticles of these fillers takes place, which causes "thickening" of their mixtures with acrylates. The modification of the fillers surfaces with the carbofunctional silanes substantially improves their dispersibility in organic media. The use of trimethoxysilanes with methacryloxypropyl or vinyl groups for the modification of nanoparticles of SiO_2 and Al_2O_3 allows to prepare transparent abrasion resistant coatings on the surface. Acrylic laquers containing nanoparticles of the fillers are utilized as top, decorative layers of furniture, as decorative layers of aluminum foils and as varnishes for floor and coatings.

Nanosphers of a mesoporous silica, functionalized with (3-aminopropyl)trimethoxysilane and a sol of gold form nanocomposites with a specific surface area around 1000 m^2/g (Botella et al., 2007) were prepared. Instead of (trialkoxy)propylsilanes containing different carbofunctional groups: amine, aldehyde, acrylate, isocyanate, thiol, ether, triacetoxy-diamine, and trialkoxysilanes containing aldehyde and nitrile groups attached to a longer alkylene "connector" were grafted on the surface of cobalt ferrite $CoFe_2O_4$. They were utilized for the preparation of water dispersions of nanoparticles with supermagnetic properties (de Palma et al., 2007).

3.3.2 Applications of silane-modified nano-fillers in thermoplastic composites

Depending on chemical structure and geometry three classes of nanoparticles were widely investigated:

- layered materials such as nanoclays (e.g. montmorillonite MMT) which were characterized by one nanometric dimension, referred to as 2D nanoparticles;
- fibrous materials, such as carbon nanotubes, which were characterized by elongated structures with two nanometric dimentions and referred to as 1D nanoparticles;
- particulate materials, such as polyhedral oligosilsesquioxane (POSS) and spherical silica nanoparticles, which were characterized by three nonometric dimension and sometimes referred to as 0D nanoparticles.

For good properties of these polymer nanocomposites it is required the homogeneous dispersion of nanoparticles in the polymer matrices. The best way to avoid aggregation is to graft polymer chains onto the particles covalently, forming organic-inorganic hybrid materials. Grafting techniques include the "grafting to", "grafting through", and "grafting

from" methods. "Grafting to" method involves the reaction of appropriate end-capped functional groups or side pendant groups in the polymers with the particles. This method is simple, but the graft density is fairly low because the diffusion of polymer chains to the surface of the particles is hindered sterically. "Grafting to" method gives relatively low grafting densities. "Grafting from" technique, in which a monomer polymerization is initiated from groups bound to particle surface is expected to lead to higher surface grafting densities, because monomer can more easily diffuse towards the reactive centre. In the "grafting through" method the surface of the particle is modified with a polymerizable group. The graft density may be relatively high as compared with the "grafting to" method, but since the monomer-modified particle is multifunctional cross-linking between polymer chains may be occur.

A variety of polymerization techniques, including conventional free radical, cationic, anionic, ring-opening, and controlled radical polymerizations (CRPs) or living radical polymerization (LRP) have been used to graft the polymer onto the particle surfaces. In comparison with the conventional radical polymerization CRPs can control the architecture, molecular weight, and molecular weight distribution, and they are simple on operation procedure and versatile on monomers in comparison with ionic polymerizations. Out of the three most common LPR methods, nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, RAFT is arguably the most applicably technique (Chrissopoulou & Anastasiadis, 2011).

3.3.2.1 Composites based on polyacrylates

Silica is the most applied filler in polymers based acrylate moieties. Polyacrylate-SiO_2 particle are usually produced by emulsion or microemulsion polymerization. The investigations on developing emulsifier-free latexes have been made. An emulsifier-free emulsion polymerization and sol-gel process were used for preparation of polyacrylate-silica hybrids in which tetraethoxysilane (TEOS) and poly(vinyl alcohol) (PVAL) were used as a silica precoursor and colloid stabilizer, respectively (Shen et al., 2009).

Surfactant-free emulsion polymerization, in which neither surface treatment for nanosilica particles nor additional surfactant or stabilizer is required is one of the methods for preparation of inorganic-organic composites. SiO_2-PMMA composite particles were prepared via conventional emulsion polymerization by the aid of acid-base interaction between the silanol groups of unmodified silica surface and amino groups of 4-vinyl-pyridine. The morphology of the composite particles could be multicore-shell, rapsberry-like or normal core-shell, depending upon the emulsifier content, monomer/silica ratio, silica particles size, and monomer feed method (Cheng et al., 2006).

Sol-gel process is often applied to prepare polymer-silica organic-inorganic hybrids, in which a nanometer size silica component is dispersed in a polymer matrix. In polymer-silica hybrids films silica component works as the hard segment in soft polymer matrix. Silane coupling agents are commonly used to achieve miscibility of the polymer and silica. Transparent polyacrylic-silica hybrid thin films were obtained from MMA, trimethylol-propanetrimathacrylate, water based monodispersed colloidal silica and coupling agent: MAPTMS. A mixture of ethylene glycol and ethyl ether was used for preventing the phase

separation of the prepared hybrid materials (Yu & Chen, 2003). PMMA-silica composites were synthesized via sol-gel reaction. The base acrylic polymers were prepared by copolymerization of MMA with MPTMS or vinyltrimethoxysilane (VTMS) and obtained copolymers were following condensed with TEOS (Brostow et al., 2008).

Covalent linking of polymer chains onto silica surface can be achieved by grafting methods. PMMA-grafted silica microparticles were synthesized via radical photopolymerization of MMA, initiated from N,N-diethyldithiocarbamate (DEDT) groups previously bound to the silica surface ("grafting from") (Derouet & Thuc, 2008). The same technique of grafting was used for preparation of poly(octadecyl acrylate)(PODA)-grafted silicas (Mallik et al., 2009). They synthesized two kinds of ATRP initiators, immobilized them on silica, and then ATRP was carried out from these initiator-grafted silicas to obtain comb-shaped polymer-grafted silica. Polymers possessing long side groups, i.e. PODA are often termed comb-shape polymers. These PODA-SiO_2 composites showed unique separation behaviour with ordered-disordered phase transition of long alkyl chains and high selectivity towards polycyclic aromatic hydrocarbons (PAHs) in the ordered (crystalline) state.

Mesoporous silicas are worthwhile fillers for polymers. The pores can be occupied by polymer chains, especially during melt blending. To realize the polymerization inside the silica pores, the pores should be empty, so the most suitable method is bulk polymerization. Perez et al. (2007) used mesoporous silica, with the interconnected porous structure where the monomer can be trapped, as a reinforcement agent for PMMA. Some polymeric chains grew into the silica and the interaction of polymer with filler was increased.

Silicone nitride (Si_3N_4) is an important ceramic material used for various applications because of its high strength, high thermal-shock resistance, low coefficient of thermal expansion, and good wear resistance. It has been proved to be an effective filler for the improvement of mechanical properties, and in particular the wear resistance of polymeric materials. To limit the nanoparticles agglomerates and improving their dispersivity in polymer matrix the surface modification of fillers is necessary. A novel macromolecular coupling agent tercopolymer BA-MMA-VTES (useful for surface modification of silicone nitride nanopowder) was synthesized. The macromolecular coupling agent bonded covalently on the surface of nano-sized Si_3N_4 particles was used for preparing of an organic coating layer (Xia et al., 2008).

3.3.2.2 Composites based on polyolefins

Isotactic polypropylene PP is a commodity polymer with widespread applications. To improve its ductility and toughness, impact modifiers like various polyolefinic elastomers (POEs) are commonly used. Inorganic fillers such as talc, silica, $CaCO_3$, $BaSO_4$, $Mg(OH)_2$ and $Al(OH)_3$ are used as reinforcing agents in these PP-blends. During the last decade PP-based nanocomposite blends, containing finely dispersed nanofillers, have received great interest. Due to the nonpolar character of the PP, functionalization of the polymer matrix and/or treatment of the nanoparticles are needed to achieve a good dispersion of the rigid nanoparticles and satisfactory mechanical properties. PP was functionalized by peroxide-initiated grafting of vinyltriethoxysilane (VTES), to give a PP-*g*-VTES derivative, which resulted in improved compatibility between the matrix and the filler. The mechanical properties of the composites were greatly enhanced in terms of tensile and flexural strength,

while impact strength was preserved when the silane-treated nanosilica was used (Bailly & Kontopoulou, 2009).

In order to promote dispersion of nano-silica in PP grafted polymerizable foaming agent p-vinylphenylsulfonylhydrazide (VPSH) onto nanoparticles was prepared via free-radical polymerization. The grafted VPSH played double role when it was melt mixed with PP. The side sulfonylhydrazide groups were decomposed with volatile gas products, which blowed up the surrounding matrix that pulled apart the agglomerated nanoparticles, while the remaining backbone of the grafted polymer helped to improve the filler-matrix interaction (Cai et al., 2006).

Aluminium anhydride is an effective flame retardant for thermoplastics for two decades. Surface treatment of mineral fillers can ease their incorporation into thermoplastic melts, such as PP. Whilst most surface modifiers can act as effective dispersant for fillers, only the silane and functionalised polymer based systems can also act as effective coupling agents in thermoplastics based composites. Liauw et al. (1995) compared three surface modifiers including a dicarboxylic acid anhydride (DAA), a silane based system and a maleanised polybutadiene (MPBD) in PP/$Al(OH)_3$ composites. At filler levels below these required for effective flame retardation, the DAA treated filler gave the composite with the best mechanical properties. At higher filler levels, i.e. above 59 % w/w, the composites based on $Al(OH)_3$ coated with the strongly coupling silane afforded the best properties. The latter treatment proved to be most effective when the polymer matrix was an impact modified PP.

A special case of nanocomposites is obtained by mixing polymers with layered silicates (nanoclays). The best known of layered silicates is montmorillonite (MMT). Layered silicates composed of 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 permits significant reinforcement at relatively low loadings if the high degree of exfoliation or intercalation is achieved. It is well known that the dispersion of clay tactoids in a polymer matrix can result in the formation of three types of composites: (1) conventional composites that contain clay tactoids dispersed simply as a segregated phase; (2) intercalated polymer-clay nanocomposites, which 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, and a separation between clay layers that depend on the polymer content of the composite. 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 layered silicate particles are usually hydrophilic and their interaction with non-polar polymers are unfavourable. There are two main objectives of surface modification on MMT: (1) to expand the interlayer space, allowing large polymer molecules to enter into the clay galleries, and (2) to improve the miscibility of MMT with the polymer to achieve a good dispersion of layered structure within the polymer matrix.

The maleic-anhydride functionalized polypropylene or polyethylene are the most commonly used to improve the interfacial bonding between the clay and respective polymers. Maleated polyethylene (PEgMA)/aminosilane compatibilizer has been very effective for preparing polyethylene-clay nanocomposites (Sanchez-Valdes et al., 2009). Silane grafting is one of methods to functionalize polyolefins, particularly for the preparation of silane-grafted water-

cross-linked polyethylene. Lu et al. (2005) prepared methacryloxypropyltrimethoxysilane (MAPTMS)-grafted PE (PE-*g*-MAPTMS) by melt grafting reaction, and then blend it with organically modified montmorillonite to make PE-*g*-MAPTMS/MMT nanocomposite.

3.3.3 Applications of POSS-modified thermoplastic polymers

POSS are a class of versatile building blocks used for the preparation of organic-inorganic hybrid polymers with designed properties. The POSS molecules can be modified into monomers, initiators, or chain transfer agents (CTA) for a living polymerization. The POSS molecule was used as monomer to prepare the POSS-containing homopolymers or copolymers (Lichtenhan et al., 1995). In recent years the preparation of the POSS-containing hybrid polymers with the novel architecture has been focused on a living and controlled-living polymerization techniques, e.g. the synthesis of the homopolymers and triblock copolymers from a POSS-based methacrylate monomer using atom transfer radical polymerization (ATRP) was carried out (Pyun et al., 2003). The star-shaped hybrid polymers were prepared via ATRP of methyl methacrylate using the octafunctional POSS molecule as an initiator (Costa et al., 2001).

Reversible addition-fragmentation chain transfer (RAFT) polymerization has a wider selectivity of the monomers containing carboxyl, amino and ionic groups and it can be used under a broad range of experimental conditions including aqueous solutions. The POSS-containing RAFT agent, prepared of minopropylisobuthyl polyhedral oligomeric silsesquioxane was used in the RAFT polymerization of N-isopropylacrylamide (NIPAM) to produce tadpole-shaped organic-inorganic hybrid poly(N-isopropylacrylamide) (PNIPAM). The same POSS-containing RAFT agent was also successively applied in the RAFT polymerization of styrene to produce the organic-inorganic hybrid homopolymers and block copolymers (Zhang et al., 2009).

Recently the living/controlled polymerization technique is combined with "click chemistry" which is based on the copper-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and alkynes. This reaction can be performed under mild conditions and it has a good tolerance of functional groups. Click chemistry has been mostly used to functionalize the end-groups or pendant groups of polymers or to built polymers with well-defined structures. The click reaction occurs between a polymer and small organic molecules or between two different polymer chains. The copper-catalyzed click reaction between alkyne-functional POSS molecules and mono-, di-, and pentafunctional azido-terminal polymers made by ATRP proceeds smoothly to form monochelic (tadpole-shaped), and ditelechelic (dumbbell-shaped) linear hybrid polymers as well as pentatelehcelic, star-shaped hybrids. The inversion of the procedure is also possible, i.e. the reaction of azido-functional POSS molecule was "clicked" to alkyne-terminated polymers (Müller et al., 2010).

It should be noted that most of the POSS molecules are intrinsically hydrophobic, while many commercial monomers are polar. Attachment of the polar group to POSS molecules make these compounds compatible with many polymers. For example oligosilsesquioxanes with poly(ethylene glycol)s, POSS-PEG monomers, because of their hydrophilic chemical structure are soluble in water and readily dispersed in polar monomers. The hydroxyl containing POSS molecules were used as an initiator in the ring-opening polymerization of lactide in the presence of a stannous catalyst.

Optical transparent films of a single POSS compound are hardly formed without cross-linking reagents due to their high symmetry and crystallinity. It could be speculated that lower the symmetries of the POSS derivatives decrease their crystallinity and would provide optical transparent film forming properties. Such kinds of materials are regarded as thermoplastic hybrids possessing low-k or refractive index.

Dumbbell-shaped trifluoropropyl substituted POSS derivatives linked by simple aliphatic chains (ethane, propane, hexane) to reduce their symmetries were synthesized. These derivatives formed optical transparent films depending on their aliphatic linkages under the low temperature, which would open the way to apply to coating on various thermally unstable materials (Araki & Naka, 2011).

3.4 Silicones and silica as flame retardant additives

Silicone-based compounds (silicones, silsesquioxanes, silicas, and silicates) usually are used not only as fillers, incorporated in the polymer matrix but also as the flame retardant additives. They are endowed with excellent thermal stability and high heat resistance, with very limited release of toxic gases during thermal decomposition. Several types of silicone polymers were applied as flame retardants in polycarbonates (Iji & Serizawa, 1998). For the PC materials modified with branched methyl- and phenylsiloxanes and end-capped by methyl groups, limiting oxygen index (LOI) increased over 35 %, whereas LOI was about 27 % for pure PC. The effect of content and block size of PDMS on LOI values was investigated for PC-*b*-PDMS copolymers. The PDMS block size influenced the dispersibility of the PDMS in the PC and the moderate PDMS dispersion (i.e. 50 nm mean inclusion size) resulted in high flame retardancy (Nodera & Kanai, 2006). Silica particles "*in situ*" formed by thermal degradation of PDMS mostly remained within the char layer. This highly oxidized char layer has the structure which prevented volatile fuel production and served as an additional thermal insulator.

The effect of silica gel structure on the flammability properties of thermoplastics has been investigated by many workers. The effect of pore volume, particle size and surface silanol concentration of silica gel in polypropylene (PP) was studied (Gilman et al., 1999). The performances of various types of silica, silica gel, fumed silica and fused silica as flame retardants in PP and polyethylene oxide were investigated. The fumed silica and silica gel accumulating near the surface acted as a thermal insulation layer and reduced the polymer concentration near the surface in contact with flame. The fused silica did not accumulate near the surface and it is mainly present in the polymer melt layer. The accumulation of silica on the surface of the burned polymer has been also observed in PMMA composites (Kashiwagi et al., 2003).

Nanometric particles in polymer matrices are known to enhance the fire resistance. POSS with general formula $(RSiO_{1.5})_8$ is an inorganic silica-like nanocage. Eight organic groups located at the corners give possibility for compatibility POSS compounds with organic polymers. These inorganic nanocages are referred to as preceramic compounds. On combustion of such polymer composite, POSS acts as a precursor forming thermally stable ceramic materials at high temperature. The incorporation of POSS in polymers modifies both the viscosity and the mechanical properties of the molten polymer. It also affects the thermal stability and fire performances by reducing the quantity of heat released upon

combustion. Metal-bearing POSS nanoparticles at tiny concentrations (ca. 1 wt. %) can markedly enhance the char yield in PP (Fina et al., 2005).

Halogen free siloxane modifiers can significantly reduce heat release characteristics of thermoplastic polyurethanes (TPUs). Segmented PUs derived from PTMO, MDI, 1,4-butanodiol were modified with secondary aminoalkyl functional PDMS via solution polymerization (Wang et al., 2000). Addition of 15 % of the PDMS allowed to reduce the cone calorimetry heat release rate by a factor of about 2/3 and hence improved fire resistance, while maintaining mechanical behaviour. It was suggested that the low surface energy characteristics of PDMS promoted migration to the air-polymer interface to form a predominately PDMS enriched surface, which was oxidized at elevated temperatures in air to a silicate-like material and this served as a protective layer, which further reduced burning of the underlaying polyurethane.

Water repellent of silicone-based materials, forming in the fire protective coatings, appear to be attractive flame-retardants, which have many advantages such as low smokes, low toxicity and halogen-free. It is known that intumescent flame retardant (IFR) system is composed of an acid source, a carbonization compound and a blowing agent. The main disadvantages of IFR system are its moisture sensitivity and poor compatibility with polymer matrix. Flammable properties of polyolefins (e.g. LOI for polypropylene is only 17 %) restrict their application in electric and electrical devices, wire and cable, public chairs, packaging films and transportations. One of the most effective methods for obtaining the halogen-free flame-retardant polyolefin is use of IFR. The effect of polydimethylsiloxane (PDMS) in IFR polypropylene containing melamine phosphate (MP) was studied (Lu et al., 2009). It was found that the values of LOI increase gradually with the increase of siloxane content in PP/MP/PDMS composites. Studies of the water resistance of these materials showed improved water leaching of MP. A polysiloxane was found to be a very effective additive for the flame retardancy and water resistance of the IFR-PP materials. An improved thermal stability for PP/MP/PDMS composites was also observed. IFR system containing polysiloxane and silane-modified SiO_2, ammonium polyphosphate (APP) in PP matrix was investigated as well (Gao et al., 2010). It was showed that both polysiloxane and silica effectively enhance the flame retardancy of the IFR-PP, and LOI values exceeded 36 %.

Silane-functionalized PP and maleic anhydride modified PP were efficient as a coupling agents for PP-aluminium hydroxide (AH) composites, in order improve the interaction between the phases. However, PP modified with vinyltriethoxysilane showed better effect on the mechanical properties (Bohrz et al., 2006).

3.5 Applications of silane-modified thermoplastics in medicine

Synthetic polymers with pendant sugar moieties are of great interest not only as simplified model of biopolymers bearing oligosaccharides, but also artificial glycoconjugates in biochemistry and medicine. A new polysiloxane copolymer with pendant glucosylthioureylene groups was prepared in reaction of amino-functionalized PDMS with glucosyl isothiocyanate. They kept the optical activity and could be used not only as biomedical and biotechnological materials, but also as a model of amphiphilic polymers. Another examples of these materials are saccharide-based polysiloxanes, i.e. PDMS grafted amylase or PDMS grafted saccharose (Zhou et al., 2004).

The CFS have also found applications for production of contact lenses. This type of membranes must to pass oxygen and this ability is determined on a base of so called *"equivalent oxygen percentage"* (EPO). A minimal value of EPO equals 5-7 %. For the soft lenses made of PDMS, with thickeness 0.2 mm, EPO equals ~20 %. Hydrophobic properties of this material can lead to a damage of a cornea, and lenses made of pure PDMS are not used. They are produced of silicone-methacrylic copolymers or the carbofunctional silanes, i.e. (methacryloxypropyl)trimethylsiloxysilane or (methacryloxypropyl)pentamethyl-disiloxane. Lenses made from these materials reach EPO value ~10 % (Arkles, 1983).

Hydrogels have been extremely useful in biomedical and pharmaceutical applications for a long time. Poly(2-hydroxyethyl methacrylate) PHEMA, a biocompatible hydrogel, can absorb a large amount of water and is used to make ophthalmic prostheses (contact or intraocular lenses), vascular prostheses, drug delivery and soft-tissue replacement. Bioactive PHEMA-silica hybrids can be produced either by addition of silica nanoparticles to HEMA monomer-PHEMA solution, or using HEMA solution and tetraethoxysilane (TEOS) (as a silica precursor) through *in situ* sol-gel processes. A hybrid monomer was prepared of HEMA and 3-aminopropyltriethoxysilane (APTS) and its polymers, and blend materials were synthesized through basic catalyzed hydrolysis and condensation of TEOS, followed by *in situ* radical polymerization of HEMA. Obtained hybrid materials were used to make bioactive scaffolds for bone engineering (Luciani et al., 2008).

Composites prepared from a silicone rubber and a hydrogel are often used as drug release materials. A silicone rubber-polyacrylamide (PAAm) composite hydrogel exhibits pH-independent swelling degree, high specific surface area and non-ionogenic character (Mashak, 2008).

Polylactides, due to their biocompatibility and biodegradability, have also been used for biomedical applications for decades. Poly(lactide-*b*-methylvinylsiloxane-*b*-lactide) triblock copolymers, in which the vinyl groups were functionalized with carboxylic acids were synthesized. At neutral pH, the carboxylate functional polysiloxane central block binds to the surface of magnetic nanoparticles, while the polylactides serve as tail blocks to provide dispersibility in polylactide solvents through interparticle steric repulsive forces. Potential application for these magnetic materials include magnetic field-directed drug delivery, magnetic cell separations and magnetic hypertherma therapy for a treatment of tumors (Ragheb & Riffle, 2008).

The permanent fungicidal and bactericidal properties of polysiloxanes bearing quaternary ammonium salt (QAS) groups have been known for five decades. Novel low surface energy antimicrobial coating, based on hybrid siloxane epoxy coatings containing QAS moieties, was capable of self-contaminating in a variety of environments. These coatings have demonstrated the ability to eliminate up to 99.9 % of pathogenic bacteria on the surface (Pant et al., 2008).

The attachment of α-helical polypeptides to the colloidal silica is interesting as the core-shell composite particles call to mind naturally existing, protein-caged materials like viruses. These hydrophobic, polypeptide-functionalized particles could be used in investigation designed to model enzyme activation or the properties of hydrophobic proteins in cell membranes.

Polyurethane elastomers since 1970s have found a wide range of biomedical applications due to a combination of good biocompatibility, good hydrolytic and oxidative biostability,

excellent mechanical properties and good processability. Commercial functionalized copolymers contain ca. 10 wt. % PDMS and are either segmented polyurethanes or polyureas that utilize polycarbonate or polyether as soft segments. They can be utilized in the manufacturing of intra-aortic balloons The anti-thrombogenic property of PDMS based polyurethanes is also utilized in artificial heart grafts, vascular grafts, implants and other such medical applications (Sheth et al., 2004).

4. Concluding remarks

Although carbofunctional silanes and polysiloxanes are known about 40 years they are still often used, and in a literature continually appear new examples of their applications for the modification of properties of polymers and other materials. The CFS have found many different applications for a preparation of polyurethane coating materials, having very good and useful properties. Bis-(3-triethoxysilyl)propyltetrasulphide) is used for the modification of natural and synthetic rubber (Sombatsompop et al., 2007), other CFS are applied for the preparation of silica in elastomers (*in situ*), and for the modification of calcium carbonate, which is used as the filler for elastomers (Zaborski, 2003).

An interest of research centers concerning the CFS and CFPS is still growing and broadens a scale of their numerous applications for modification of polymers. They have a great technological meaning. So far the carbofunctional silanes and polysiloxanes have found many practical applications: these first – mainly as adhesion promoters, polymer modifiers, and crosslinking agents for polyolefins, these latter - in the synthesis of different silicone-organic copolymers with very profitable properties. Perspectives of their further applications seem to be very promising, and especially for the modification of properties of different organic polymers, not only thermoplastics, but also elastomers, chemically hardenable polymers and thermosetting plastics. The carbofunctional silanes are more often used in practice than CFPS. A main barrier in applications of carbofunctional polysiloxanes on a bigger scale is a high cost of their production. However the chemical modification of polymers with CFPS has a very profitable influence on properties of the modified polymers.

In this Chapter we have been able to describe only a part of results concerning applications of silanes, siloxanes and silicate modified thermoplastic polymers.

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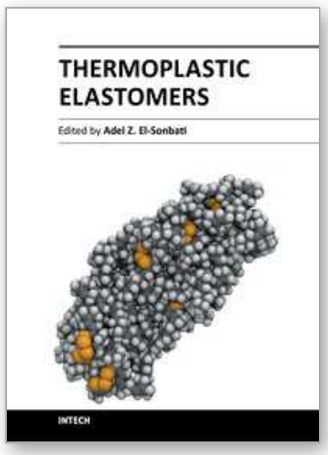
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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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