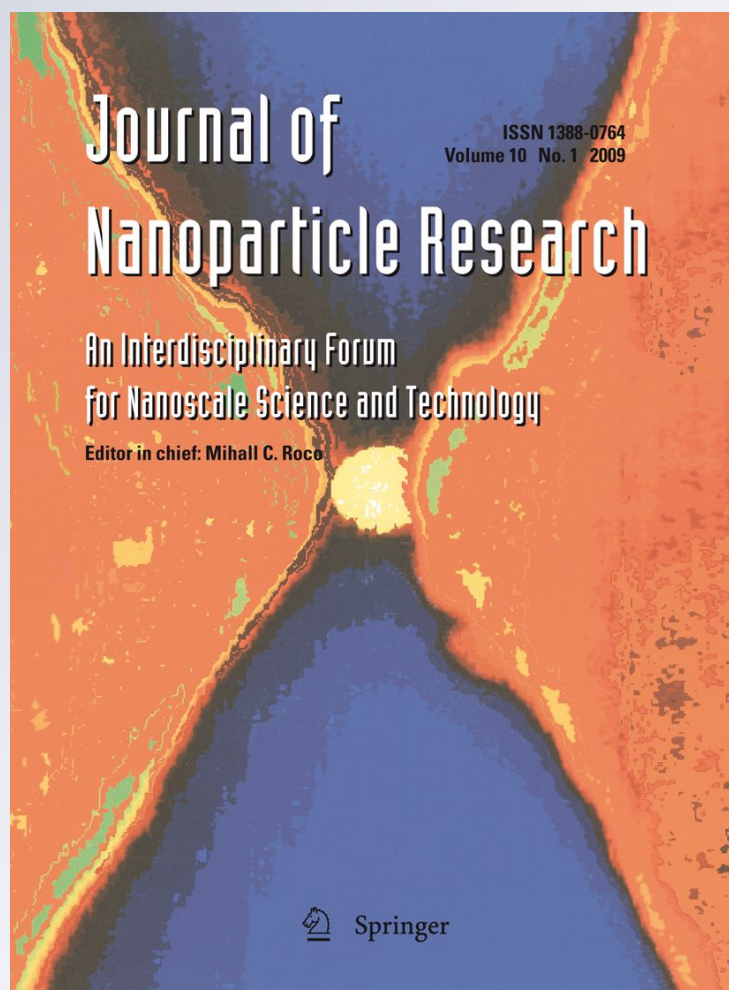*Polymer nanocomposite coatings based on polyhedral oligosilsesquioxanes: route for industrial manufacturing and barrier properties*

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RESEARCH PAPER

Polymer nanocomposite coatings based on polyhedral oligosilsesquioxanes: route for industrial manufacturing and barrier properties

**Ferdinand Männle · Terje Rosquist Tofteberg ·
Morten Skaugen · Huaitian Bu · Thijs Peters ·
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Abstract A route to a large variety of functionalized POSS compounds by a two-step procedure has been developed. Up-scaling to high volume industrial applications is feasible. In the first step, an amino-functionalized silane such as 3-aminopropyltriethoxy silane is converted to amino-functionalized POSS (amine-POSS) by a sol–gel process. In the second step, the amine groups of amine-POSS are converted by state-of-the-art amine chemistry. A large number of reactants including carboxylic acids, esters, anhydrides, isocyanates, carbonates, epoxides, and acrylates as well as reactants suitable for nucleophilic substitution can be applied. Conversion of an amine-POSS with hexanoic acid leads to an amide-POSS. Amine chemistry can usually be performed under mild conditions, which suppresses degradation and/or cross-linking reactions of the amine-POSS during the conversion. MALDI-TOF mass spectroscopy and dynamic light scattering (particle size: 3–6 nm) have been applied to prove the conversion of an amine-POSS to an amide-POSS. ^{1}H-NMR and TGA-MS prove the presence of amide-POSS and its thermal stability. Gas barrier properties of nanocomposite coatings based on functionalized POSS are characterized.

Keywords Nanocomposite · POSS · Synthesis · Hybrid polymer · Industrial manufacturing · Barrier properties

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Introduction

Organic/inorganic hybrid polymers based on polyhedral oligomeric silsesquioxanes (POSS) face increasing interest. POSS polymers are composed of a robust silicon-oxygen framework with a diameter of about 1.5 nm that can be functionalized with a variety of organic substituents. Appropriate functionalization of POSS polymers allows their incorporation in traditional polymer products. A considerable number of applications in thermoplastics (Fina et al. 2008; Iwamuraa et al. 2009; Kim et al. 2008; Liu et al. 2008; Sanchez-Soto et al. 2009; Wan et al. 2009; Zhang et al. 2009; Zhou et al. 2008), thermosets (Glodek et al. 2008; Li et al. 2008; Zhang et al. 2007c, d, e), coatings (Amerio et al. 2008; Kim et al. 2009; Mabry et al. 2008), porous materials (Su and Chen 2009; Zhang et al. 2007a), medicine (Kannan et al.

2005; Kidane et al. 2007; Wheeler et al. 2006; Wu and Mather 2009), and light emitting polymers (Xiao et al. 2010) have been published recently. POSS as a component in polymer blends is used to improve tensile properties, impact strength, heat stability, gas barrier properties, and rheological properties. For most applications, POSS compounds are manufactured by controlled hydrolysis and condensation of suitable functionalized silanes (sol–gel process). In order to obtain the desired organic branches on the POSS molecules, silanes available with exactly these organic groups have to be used (Haas and Rose 2003). A major drawback of this manufacturing method is the need of specifically modified silanes for each type of POSS. Since few organic silanes are produced in a large scale, the use of this manufacturing method for high volume industrial applications such as food packaging or automotive is limited. In a few cases, the organic branches on POSS molecules can be further modified by selected chemical reagents. However, these processes yield a rather limited selection of modified POSS compounds (Lichtenhan et al. 1995; Schwab and Lichtenhan 1998). A comprehensive review on synthesis and properties of POSS has recently been published (Cordes et al. 2010). However, none of the preparation methods in this review has been up-scaled for high volume industrial applications.

Four patent applications have been filed in 2004 and 2005 disclosing the preparation and use of polybranched organic/inorganic hybrid polymers (Männle et al. 2004a, b, c, 2005). The polybranched organic/inorganic hybrid polymers are synthesized by controlled hydrolysis and condensation of 3-aminopropyltriethoxy silane (γ-APS) followed by the development of the organic branches using state-of-the-art amine chemistry. The chemical structure of the obtained hybrid polymers has not been investigated and published in the patent work or previous publications (Pilz et al. 2009a, b). In this publication, we fill this gap by studying a typical synthesis of polybranched organic/inorganic hybrid polymers to show that mainly POSS compounds are formed. A novel route to a large variety of functionalized POSS compounds by a two step procedure is therefore feasible. In the first step, an amino-functionalized silane is converted to amino-functionalized POSS (amine-POSS) by a sol–gel process. In the second step, the organic branches of amine-POSS are extended by state-of-the-art amine chemistry.

From an industrial point of view, POSS products can be interesting components in polymer products if their benefit is not spoiled by too high manufacturing costs. The use of low cost organic commodities such as fatty acids decreases the manufacturing costs. Very recently, a POSS containing alkyd paint with reduced VOC and improved weathering resistance in northern climate has been introduced to the market (Helland et al. 2009). Barrier properties of polymer nanocomposite coatings based on functionalized POSS are now characterized by gas transmission rates of oxygen and helium to show the potential of those coatings for industrial packaging applications.

Experimental section

Synthesis of polyhedral oligosilsequioxanes

Step 1

Amine-POSS: 221.4 g (1.00 mol) 3-aminopropyltriethoxysilane is placed in a 1000 mL flask equipped with reflux cooler and magnetic stirring under nitrogen atmosphere. A mixture of 64.9 g (0.60 mol) 1-propoxy-2-propanol and 22.5 g (1.30 mol) water is added. The mixture is warmed up and refluxed at 80 °C for 45 min. Thereafter, volatile products and the solvent are removed by vacuum distillation with the final pressure 20 mbar and temperature 150 °C. The product is cooled to 120 °C and diluted with 1-propoxy-2-propanol to yield a 50% solution of amine-POSS in 1-propoxy-2-propanol.

Step 2

Amide-POSS: 63.9 g (0.55 mol) hexanoic acid (reactant) and 63.9 g 1-propoxy-2-propanol are heated to 150 °C. 118 g of a 50% solution of amine-POSS in 1-propoxy-2-propanol (0.50 mol amine-POSS) is added within 30 min, while water as well as 1-propoxy-2-propanol are distilled off. After the addition of amine-POSS is finished, the pressure is stepwise reduced to 20 mbar, and water and 1-propoxy-2-propanol are distilled of. To remove residues of 1-propoxy-2-propanol, the product is dissolved in ethanol under heating, and the solvent is removed by vacuum drying (final pressure: 10^{-3} mbar).

Characterization of polyhedral oligosilsesquioxanes

^{1}H-NMR (300 MHz, Varian Gemini, DMSO-d_6)

–Si–CH_2– 0.53 ppm, –CH$_2$–CH_3 0.85 ppm, –C(O)–CH$_2$–CH_2–/–CH_2–CH$_3$ (overlapping) 1.24 ppm, –Si–CH$_2$–CH_2–/-C(O)–CH$_2$–CH_2– (overlapping) 1.46 ppm, –C(O)–CH_2– 2.05 ppm, –Si–CH_2–CH$_2$–CH$_2$– 3.00 ppm, –HN–C(O)– 7.84 ppm.

MALDI-TOF

A solution of 1% v/v of amide-POSS in 2-methoxy propan-1-ol was mixed in a ratio 1:1 v/v with matrix solution. The matrix solution consisted of 15 mg/mL 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid (sDHB, Bruker Daltonics, Bremen, Germany) dissolved in a mixture of trifluoroacetic acid (0.1% v/v), de-ionized water (49.9% v/v), and ethanol (50% v/v). The so prepared sample was applied directly on the MALDI target (Bruker Daltonics ground steel). The instrument (Ultraflex TOF/TOF, Bruker Daltonics) was operated at an acceleration voltage 25 kV with delayed ion extraction 40 ms using a 337 nm N$_2$ laser.

Dynamic light scattering

A commercial LLS spectrometer (ALV/CGS-8F) equipped with four ALV 5000/E multiple-τ digital time correlator and a cylindrical 22 mW HeNe-laser ($\lambda_0 = 632.8$ nm) was used. The beam was focused on the sample cell (10 mm NMR tubes, Wilmad Glass Co, of highest quality) through a temperature-controlled cylindrical quartz container filled with a refractive index matching liquid *cis*-decalin, with the temperature controlled to within ±0.05 °C. The details of LLS instrumentation and theory can be found elsewhere (Beheshti et al. 2008; Chu 1991). DLS measurements were performed on 10 wt% solutions of amine-POSS and amide-POSS in 1-propoxy-2-propanol to determine the hydrodynamic radii of the two particles. The hydrodynamic radius of the particle in solution was calculated according to the Stokes–Einstein relation, using the diffusion coefficients deduced from the correlation functions.

Thermogravimetric analysis and mass spectroscopy (TGA–MS)

TGA–MS was performed on a STA 449 F1-QMS (Netzsch, Germany). The heating rate was 2 °C/min under nitrogen atmosphere. The QMS mass range is 300 amu with a resolution of >0.5 amu.

Gas barrier measurements

The oxygen transmission rate (OTR) has been measured at standard conditions (23 °C, 50% RH) with an OX-TRAN® Model 2/10. Measurements to determine helium transmission rate (HeTR) were performed in an in-house built membrane-like set-up. A back pressure controller (Bronkhorst High-Tech) was used to pressurize the helium feed up to 2.0, 3.0, and 4.0 bar, while Argon was applied at the permeate side. A μ-GC (Varian CP4900) was employed to monitor the permeate composition. Fluxes were calculated from the measured permeate He concentration and the calibrated flow of argon sweep gas.

Fig. 1 Synthesis of amine-POSS by a sol–gel process (step 1)
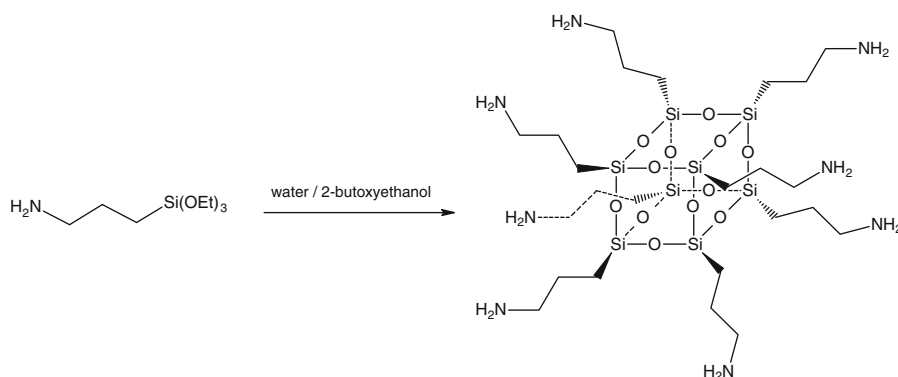
Results and discussions

Polyhedral oligosilsesquioxanes: amine-POSS and amide-POSS

Amine-POSS

The conversion of 3-aminopropyltriethoxy silane (APS) to amine-POSS is shown in Fig. 1. In order to reduce the amount of unreacted Si–OCH$_2$–CH$_3$ and Si–OH intermediates, the amine-POSS is heated in 1-propoxy-2-propanol to 150 °C, and the solvent is removed by vacuum distillation. The amount of free amine groups is measured as amine equivalents by titration with hydrochloric acid. The product has an amine number of 118 g/eq which is quite close to the calculated value of 111 g/eq. The deviation can be explained by a suppressed degradation of amine groups during the process and the presence of solvent residues.

Amide-POSS

Figure 2 shows the conversion of amine-POSS with hexanoic acid to amide-POSS. The product is soluble in mixtures of water and 2-butoxyethanol, and titration shows no unreacted amine groups. Instead of hexanoic acid, a large number of reactants including other carboxylic acids, esters, anhydrides, isocyanates, carbonates, epoxides, and acrylates as well as reactants suitable for nucleophilic substitution can be applied.

This opens up versatile applications and materials based on POSS. Amine chemistry can usually be performed under mild conditions which limit the degradation and/or cross linking of amine-POSS.

MALDI-TOF

The method of choice to measure the molecular weight of POSS compounds is MALDI-TOF. This has been demonstrated previously (dell' Erba et al. 2003; Manson et al. 2001; Smentkowski et al. 2006; Sheen et al. 2008).

MALDI-TOF of amide-POSS (Fig. 3) shows the presence of T$_8$, T$_{10}$, and T$_{12}$ POSS which is in compliance with earlier findings (dell' Erba et al. 2003; Zhang et al. 2007b).

Larger POSS molecules are present in minor amounts. The assignment of the MALDI-TOF peaks is based on the assumption that the amide-POSS partly looses hexanoyl groups during laser desorption ionization. A possible explanation is the formation of agglomerates due to strong hydrogen bondings between the amide groups which partially lead to bond cleavage during desorption. Hydrolysis during sample preparation and desorption is unlikely since these processes are performed within 5 min. On this background, we assume that each peak can be attributed to a molecule on the form T$_{2m}$–R$_n$, where R is CO(CH$_2$)$_4$CH$_3$. For all m equal 4 to 10 and for all n equal 1 to m, the theoretical isotope distribution of the molecule
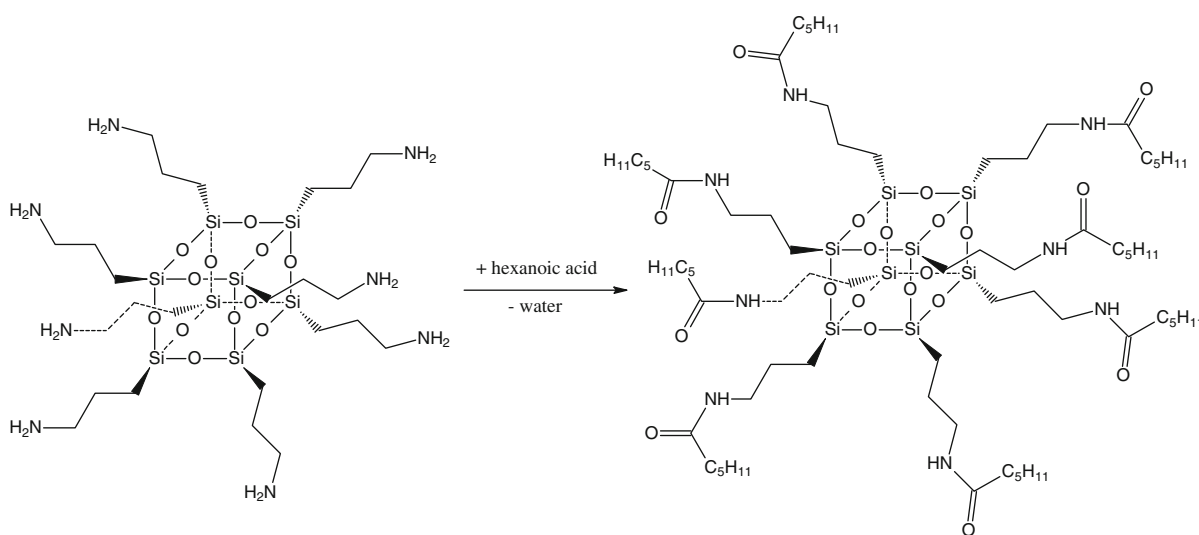
Fig. 2 Synthesis of amide-POSS by reaction of amine-POSS with hexanoic acid (step 2)

Fig. 3 MALDI-TOF mass spectrum of amide-POSS (*blue*) compared with the theoretical isotope distribution (*red*)
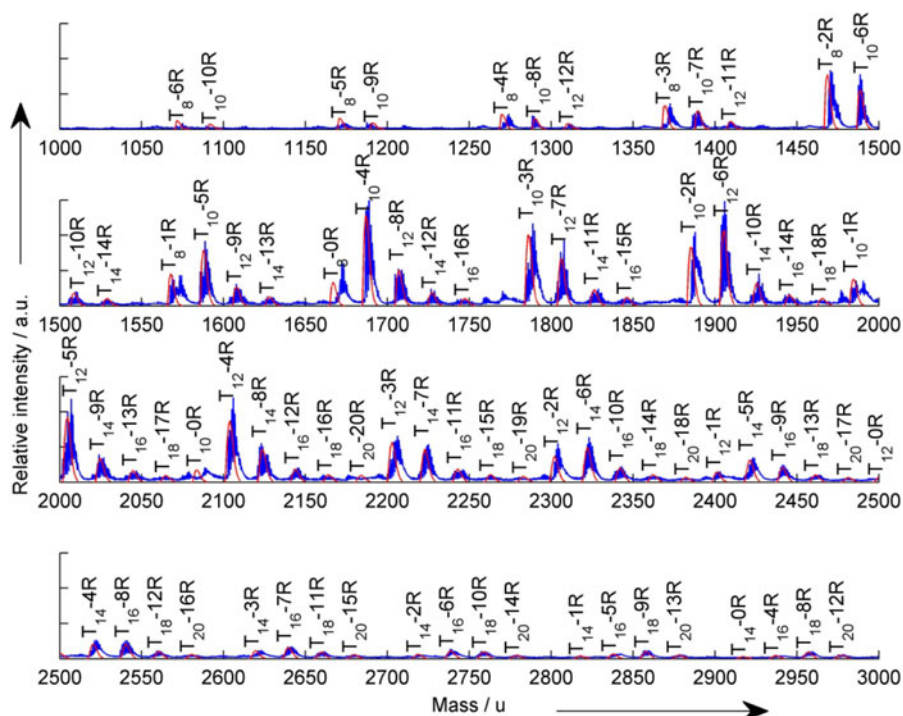
T_{2m}–R_n is calculated and shown together with the mass spectrum in Fig. 3. It can be seen that all peaks in the spectrum can be accounted for by this assumption.

The integral of each peak is shown as a function of n and m (Fig. 4). It can be seen that the most common products are the T_{10} and the T_{12}, but also smaller amounts of T_8, T_{14}, and T_{16} are present. It can also be seen that within each T_{2m} series the most abundant molecule is missing approximately half of the R
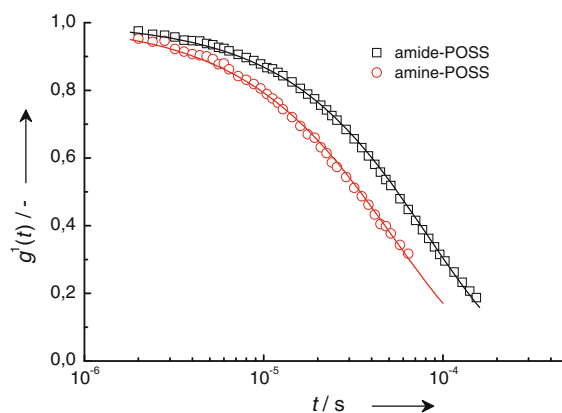
groups, with the abundance falling to each side of the central value.

Dynamic light scattering

The particle size increase resulting from the conversion of amine-POSS to amide-POSS has also been demonstrated by dynamic light scattering. Figure 5
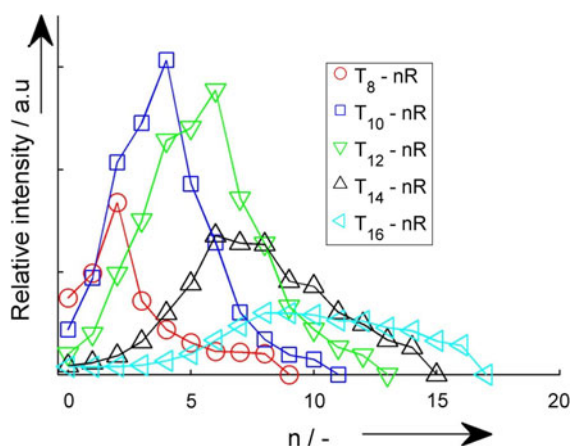
Fig. 4 Integrated intensity of the peaks based on the MALDI-TOF mass spectrum of amide-POSS as shown in Fig. 3

Fig. 5 DLS correlation functions for amine-POSS and amide-POSS in 1-propoxy-2-propanol—*solid lines* show a fit of the correlation function to a stretched exponential function log $g^1(t) = -(t/\tau_f)^\beta$

depicts the correlation functions of amine-POSS and amide-POSS at a scattering angle of 90°. As can be seen from Fig. 5, the correlation function shifts to longer times when the amine-POSS was modified by hexanoic acid and converted into amide-POSS. This indicates that the diffusion of the particles becomes slower. Both systems are diffusive with narrow distribution of relation time, implying the homogeneous size distributions of both amine-POSS and amide-POSS. The diffusion coefficient (D_m) was then calculated as described in the Experimental section. The hydrodynamic radius of amine-POSS and amide-POSS are 1.7 and 2.7 nm, respectively. The difference is in good compliance with the length of a hexanoyl group which is between 0.8 and 0.9 nm. Therefore, the increase indicates the conversion of amine groups to the considerably larger hexanoic amide groups.

^{1}H-NMR

The ^{1}H-NMR spectrum in Fig. 6 indicates a high purity of the amide-POSS. Visible impurities are small amounts of ethanol which was used for sample preparation and the reactant hexanoic acid which was used in excess. The α-CH$_2$-resonance of hexanoic acid in the presence of amide-POSS is shifted to high field

which can be explained by a different chemical environment due to hydrogen bonding (Limbach 2007).
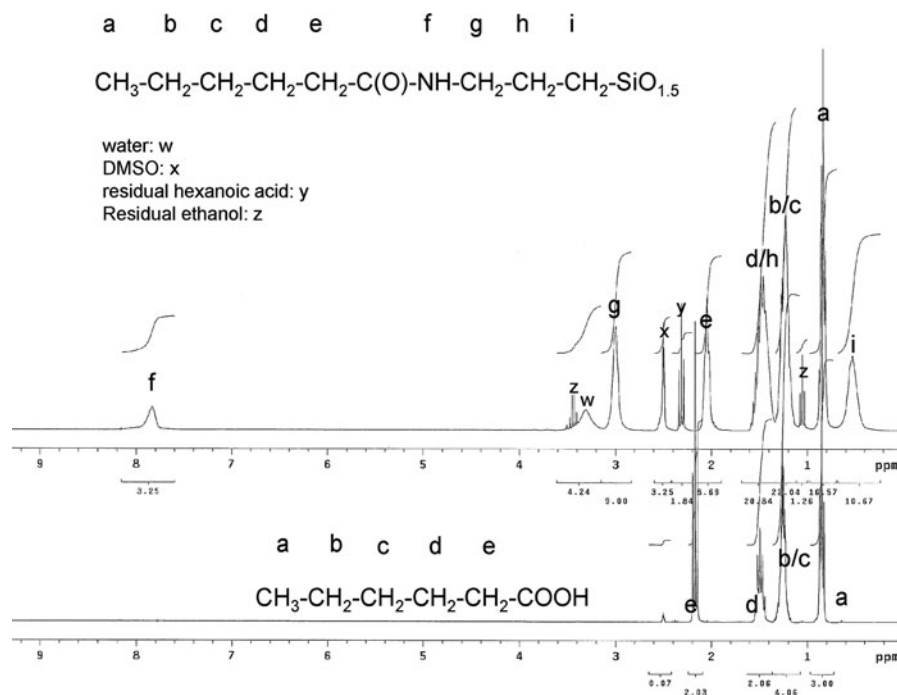
TGA–MS

The presence of free hexanoic acid is also shown in the TGA–MS analysis (Fig. 7). Water ($m/z = 18$) and hexanoic acid ($m/z = 60$) are evaporated below 200 °C. Severe degradation starts right below 400 °C. The DSC-line between the mass traces shows that both processes are endothermic. Thermal stability is of the essence when POSS is blended into polymers using melt processes.

Selection of functionalized POSS prepared by the two-step procedure

Several types of functionalized POSS have been prepared by the two-step procedure and presented in Table 1.

The products are registered under the trademark FunzioNano®. Amine-POSS has been prepared as described above in synthesis step 1. The reactants have been added similar to the procedure described in synthesis step 2.

Fig. 6 ^{1}H-NMR spectra of reactant hexanoic acid (*below*) and amide-POSS (*above*)
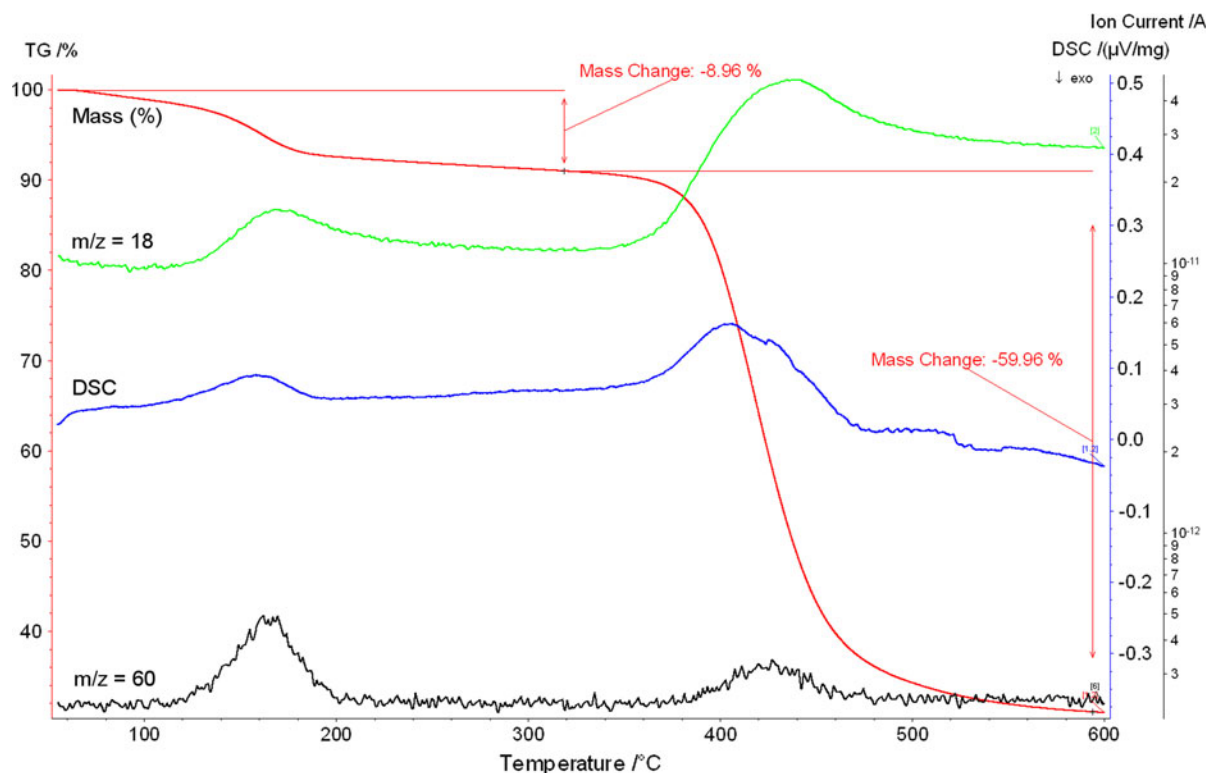
Fig. 7 TGA–MS analysis of amide-POSS

Table 1 Selected qualities of FunzioNano®

Derivative	Reactant	Chemical functionality
Amine-POSS	None	Primary amine
FunzioNano-1	Hexanoic acid	Amide
FunzioNano-2	Mixture of unsaturated fatty acids	Amide
FunzioNano-3	Salicylic acid	Amide
FunzioNano-4	Glycidyl methacrylate	Tertiary amine/acrylic cross linking

The most important factor of the manufacturing costs is the price of the silane. A typical industrial bulk price for 3-aminopropyltriethoxy silane is currently 6 EUR/kg. The reactants are normally less expensive and contribute with 1-2 EUR/kg. Typical manufacturing costs based on the raw materials of the FunzioNano® in Table 1 are about 4 EUR/kg.

Gas barrier properties of polymer nanocomposite coatings based on POSS

The gas barrier properties of polymer materials are very much influenced by the presence of aromatic moieties, polar groups such as hydroxyl groups and the degree of cross linking. The OTR of the aromatic polyester polyethylene terephthalate (PET) is considerably lower as the OTR of the aliphatic polyester poly lactic acid (PLA). The OTR of the partial polar ethylene vinyl alcohol copolymers (EVOH) is significantly lower than the OTR of the non-polar polyethylene. Finally, the gas barrier properties of cross-linked polyethylene are superior to those of a similar non cross-linked polyethylene (Massey 2003).

The synthesis of POSS as described above makes the combination of different structural elements on a single core feasible. The different structural elements can exhibit different influence on the gas barrier properties of the POSS material. In this context,

FunzioNano-2 consists mainly of non-polar aliphatic hydrocarbon moieties resulting from the mixture of unsaturated fatty acids which have been used as reactant. Aliphatic hydrocarbon chains provide a low gas barrier. However, the non-polar aliphatic hydrocarbon moieties are connected to the POSS backbone by polar amide bonds. Amide bonds are known to increase the gas barrier properties of a material significantly which leads to a significantly lower transmission of oxygen or helium in polyamides compared to polyethylene. Table 2 shows that the presence of the amide bond is less important for gas barrier properties of FunzioNano-2 than the aliphatic hydrocarbon moieties. The OTR of FunzioNano-2 is comparable to polyethylene rather than to polyamide.

POSS molecules without long chain aliphatic hydrocarbon moieties can provide a better barrier against oxygen. Neither FunzioNano-3 nor Funzio-Nano-4 contains such moieties. A mixture of FunzioNano-3 and FunzioNano-4 has been applied to a thermoplastic surface and cured at moderate temperature (48 h, 60 °C). The application of the FunzioNano® mixture as a barrier coating (thickness: 20 μm) onto a compression molded HDPE sample (high density polyethylene; film thickness: 120 μm) reduces the OTR from 150 cm^3/m^2 day to 8 cm^3/m^2 day (Fig. 8).

FunzioNano-3 contains aromatic moieties, amide bonds, and hydroxyl groups which lead to an increased gas barrier. FunzioNano-4 contains hydroxyl groups and additionally acrylic double bonds which are cross linked during the curing procedure. As a result, the OTR is significantly reduced by the coating.

The use of amine-POSS as cross-linking agent in epoxy systems (Table 3) can increase the cross-linking density (Li et al. 2005; dell' Erba and Williams 2008). The hardener component of the selected epoxy resin is modified by amine-POSS (Simon and Männle 2004). Stoichiometric mixing ratios were used. All components are mixed by moderate agitation, and the ready-to-handle resins are applied by tape casting on non-adherent polymer

Table 2 OTR and HeTR in a film of FunzioNano-2 compared to commercial materials with similar functional groups

Material	OTR (cm^3 20 μm/m^2 day)	HeTR (cm^3 20 μm/m^2 day)	Rel. humidity (%)[g]
LLDPE[a]	18200[e]	36900[e]	0/0
LDPE[b]	12000[f]	28000[f]	0/0
PA-66 (non-oriented)[c]	40[f]	2960[f]	50/50
PA-12 (BOPA-12)[d]	43[e]	2306[e]	50/0
FunzioNano-2	4650[e]	49000[e]	0/0

[a] Linear low density polyethylene

[b] Low density polyethylene

[c] Polyamide

[d] Bis-oriented polyamide

[e] Measured with the methods described in Experimental section "Gas barrier measurements."

[f] Massey (2003)

[g] The first number refers to OTR and the second number refers to HeTR

Fig. 8 OTR [cm^3/m^2 day] of a FunzioNano® coated HDPE film

Table 3 Composition of modified epoxy samples: all components in (mass%)

Sample	Resin bisphenol-A MW 380 g/mol	Difunctional reactive diluent neopentyl glycol diglycidyl ether MW 216 g/mol	Amine hardener polyamine-adduct	Amine hardener amine-POSS
Epoxy 1	65.1	0.0	28.7	6.2
Epoxy 2	58.4	6.5	35.1	0.0
Epoxy 3	57.9	6.4	29.4	6.3

Fig. 9 HeTR of epoxy films containing amine-POSS
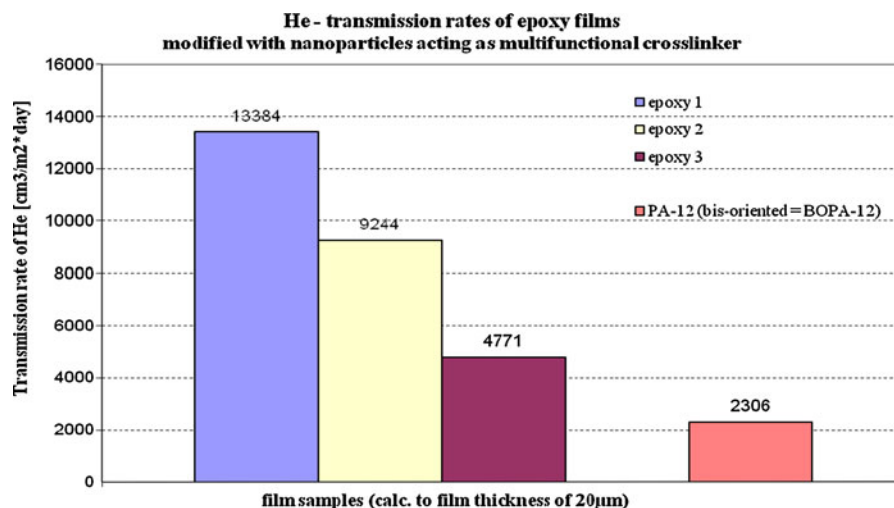
substrates in wet film thickness of 200 μm. The very smooth coating layers are cured under ambient conditions.

Higher cross-linking density leads to an increased gas barrier. In addition, during cross linking the reactive diluent yields more OH-groups per mass unit than the epoxy resin due to lower molecular weight. Thus, this increases the gas barrier properties.

Highly cross-linked nanoparticle-modified epoxy coatings can give gas barrier properties close to the level of BOPA-12 (Fig. 9) and have good adhesion to a variety of substrate materials. This could make two layer flow pack barrier films such as epoxy coated bis-oriented polypropylene (BOPP) feasible. In addition, the modified epoxy coatings show high transparency and excellent UV resistance (Pilz et al. 2009a).

Summary and conclusions

It has been shown that a two-step synthesis of modified POSS is feasible. The basic POSS structure with free amine groups is formed in the first step. The modification of these amine groups using state-of-the-art amine chemistry is done in the second step without degrading the POSS structure. Therefore, a large variety of functionalized POSS compounds can be yielded by this method.

From an industrial point of view, POSS products can be interesting components in polymer products if their benefit is not spoiled by too high manufacturing costs. The use of low cost organic commodities such as fatty acids decreases the manufacturing costs.

Very recently, a POSS containing alkyd paint with reduced VOC and improved weathering resistance in northern climate has been introduced to the market. This would not have been possible with only silanes as raw materials for POSS synthesis.

Several types of POSS which were made by the two-step synthesis have been applied in nanocomposite coatings. Gas barrier properties against oxygen and helium have been improved. Good adhesion to a variety of substrate materials combined with low gas transmission rates makes these POSS types to an interesting component in industrial packaging developments.

References

Amerio E, Sangermano M, Colucci G, Malucelli G, Messori M, Taurino R, Fabbri P (2008) UV curing of organic-inorganic hybrid coatings containing polyhedral oligomeric silsesquioxane blocks. Macromol Mater Eng 293:700–707

Beheshti N, Zhu K, Kjøniksen A, Nyström B (2008) Interaction behaviors in aqueous solutions of negatively and positively charged hydrophobically modified hydroxyethylcellulose in the presence of an anionic surfactant. Colloids Surf A Physicochem Eng Asp 328(1–3):79–89

Chu B (1991) Laser light scattering: basic principles and practice. Academic Press, Boston

Cordes DB, Lickiss PD, Rataboul F (2010) Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes. Chem Rev 110:2081–2173

dell' Erba IE, Williams RJJ (2008) Epoxy networks modified by multifunctional polyhedral oligomeric silsesquioxanes (POSS) containing amine groups. J Therm Anal Calorim 93(1):95–100

dell' Erba IE, Fasce DP, Williams RJJ, Erra-Balsells R, Fukuyama Y, Nonami H (2003) Poly(silsesquioxanes) derived from the hydrolytic condensation of organotrialkoxysilanes containing hydroxyl groups. J Organomet Chem 686:42–51

Fina A, Bocchini S, Camino G (2008) Catalytic fire retardant nanocomposites. Polym Degrad Stab 93:1647–1655

Glodek TE, Boyd SE, McAninch IM, La Scala JJ (2008) Properties and performance of fire resistant eco-composites using polyhedral oligomeric silsesquioxane (POSS) fire retardants. Compos Sci Technol 68:2994–3001

Haas K, Rose K (2003) Hybrid inorganic/organic polymers with nanoscale building blocks: precursors, processing, properties and applications. Rev Adv Mater Sci 5:47–52

Helland T, Marstokk O, Männle F, Simon CR, Yang J (2009) Binder for air-drying paint comprising nanoparticle organically modified metal oxides. WO2009113876

Iwamuraa T, Adachib K, Sakaguchia M, Chujo Y (2009) Synthesis of organic–inorganic polymer hybrids from poly(vinyl chloride) and polyhedral oligomeric silsesquioxane via CH/π interaction. Prog Org Coat 64:124–127

Kannan RY, Salacinski HJ, Butler PE, Seifalian AM (2005) Polyhedral oligomeric silsesquioxane nanocomposites: the next generation material for biomedical applications. Acc Chem Res 38(11):879–884

Kidane AG, Edirisinghe MJ, Bonhoeffer P, Seifalian AM (2007) Flow behaviour of a POSS biopolymer solution. Biorheology 44:265–272

Kim KH-U, Bang YH, Choi SM, Yoon KH (2008) Polyhedral oligomeric silsesquioxane-reinforced polyurethane acrylate. Compos Sci Technol 68(13):2739–2747

Kim EH, Myoung SW, Jung YG, Paik U (2009) Morphology and mechanical properties of PET by incorporation of amine-polyhedral oligomeric silsesquioxane. Prog Org Coat 64(2–3):205–209

Li H, Yu D, Zhang JQ (2005) A novel and facile method for direct synthesis of cross-linked polysiloxanes by anionic ring-opening copolymerization with Ph12-POSS/D4/Ph8D4. Polymer 46(14):5317–5323

Li Q, Hutcheson SA, McKenna GB, Simon SL (2008) Viscoelastic properties and residual stresses in polyhedral oligomeric silsesquioxane-reinforced epoxy matrices. Polym Sci Polym Phys 46(24):2719–2732

Lichtenhan JD, Otonari YA, Cam MJ (1995) Linear hybrid polymer building blocks: methacrylate-functionalized polyhedral oligomeric silsesquioxane monomers and polymers. Macromolecules 28(24):8435–8437

Limbach HH (2007) Single and multiple hydrogen/deuterium transfer reactions in liquids and solids. In: Hynes JT, Klinman J, Limbach HH, Schowen RL (eds) Hydrogen transfer reactions, vol 1. Wiley-VCH, Weinheim, pp 135–221 and references cited therein

Liu YR, Huang YD, Liu L (2008) Influence of methacryl polyhedral oligomeric silsesquioxane on the thermal and mechanical properties of methylsilicone resin. J Appl Polym Sci 110(5):2989–2995

Mabry JM, Vij A, Iacono ST, Viers BD (2008) Fluorinated polyhedral oligomeric silsesquioxanes (F-POSS). Angew Chem Int Ed 47(22):4137–4140

Männle F, Simon CR, Beylich J, Redford K (2004a) Poly-branched, organic/inorganic hybrid polymer and method for its manufacture. WO2005100449

Männle F, Simon CR, Beylich J, Larsen ÅG, Hauge RP, Kleppe EA, Rødseth KR (2004b) Polymer composition. WO2005100469

Männle F, Simon CR, Beylich J, Sommer B, Hinrichsen EL, Andreassen E, Olafsen K, Redford K, Didriksen T (2004c) Method for the manufacture of polybranched organic/inorganic hybrid polymers. WO2005100450

Männle F, Rødseth KR, Bu H (2005) Light protective additive based on organic/inorganic hybrid polymer method for its manufacture and use thereof. WO2007053024

Manson BW, Morrison JJ, Coupar PI, Jaffrès P-A, Morris RE (2001) Synthesis of aldehyde functionalised polyhedral oligomeric silsesquioxanes. J Chem Soc Dalton Trans 1123–1127

Massey LK (2003) Permeability properties of plastics and elastomers: a guide to packaging and barrier materials. In: Massey LK (ed) Plastics design library. Norwich, New York

Pilz M, Helland T, Simon CR, Yang J, Männle F, Bu H, Marstokk O (2009a) Epoxy coatings based on nanotechnology by using organic inorganic hybrid polymers. In: Proceedings of 19th SLF Congress, Sandefjord, 07–08 Sep 2009

Pilz M, Männle F, Simon CR, Trevor SL, Bu H, Tanem BS (2009b) New method for improving properties of polymer composites by using organic inorganic hybrid polymers. Solid State Phenom 151:10–16

Sanchez-Soto M, Schiraldi DA, Illescas S (2009) Study of the morphology and properties of melt-mixed polycarbonate–POSS nanocomposites. Eur Polym J 45(2):341–352

Schwab JJ, Lichtenhan JD (1998) Polyhedral oligomeric silsesquioxane (POSS)-based polymers. Appl Organomet Chem 12(10/11):707–713

Sheen Y-C, Lu C-H, Huang C-F, Kuo S-W, Chang F-C (2008) Synthesis and characterization of amorphous octakis-functionalized polyhedral oligomeric silsesquioxanes for polymer nanocomposites. Polymer 49(18):4017–4024

Simon CR, Männle F (2004) Epoxy resin curing agent for enhanced wear resistance and weatherability of cured materials. WO2004035675

Smentkowski VS, Duong HM, Tamaki R, Keenan MR, Ohlhausen JAT, Kotula PG (2006) Using time-of-flight secondary ion mass spectrometry and multivariate statistical analysis to detect and image octabenzyl-polyhedral oligomeric silsesquioxane in polycarbonate. Appl Surf Sci 253:1015–1022

Su H-W, Chen W-C (2009) Preparation of nanoporous poly (methyl silsesquioxane) films using core-shell silsesquioxane as porogen. Mater Chem Phys 114(2–3): 736–741

Wan C, Zhao F, Bao X, Kandasubramanian B, Duggan M (2009) Effect of POSS on crystalline transitions and physical properties of polyamide-12. J Polym Sci B Polym Phys 47(2):121–129

Wheeler PA, Fu BX, Lichtenhan JD, Weitao J, Mathias LJ (2006) Incorporation of metallic POSS, POSS copolymers, and new functionalized POSS compounds into commercial dental resins. J Appl Polym Sci 102(3): 2856–2862

Wu J, Mather PT (2009) POSS polymers: physical properties and biomaterials applications. Polym Rev 49(1):25–63

Xiao Y, Lu X, Zhang X, He C (2010) Synthesis and optical characteristics of organic light-emitting dot based on well-defined octa-functionalized silsesquioxane. J Nanopart Res 12(8):2787–2798

Zhang L, Abbenhuis HCL, Yang Q, Wang Y-M, Magusin PCMM, Mezari B, van Santen RA, Li C (2007a) Mesoporous organic–inorganic hybrid materials built using polyhedral oligomeric silsesquioxane blocks. Angew Chem Int Ed 46(26):5003–5006

Zhang X, Huang Y, Wang T, Hu L (2007b) Effects of silsesquioxane coating structure on mechanical interfacial properties of carbon fibre/polyarylacetylene composites. J Mater Sci 42(13):5264–5271

Zhang Z, Gu A, Liang G, Ren P, Xie J, Wang X (2007c) Thermo-oxygen degradation mechanisms of POSS/epoxy nanocomposites. Polym Degrad Stab 92(11):1986–1993

Zhang Z, Liang G, Wang J, Ren P (2007d) Epoxy/POSS organic–inorganic hybrids: viscoelastic, mechanical properties and micromorphologies. Polym Compos 28(2): 175–179

Zhang Z, Liang G, Wang X (2007e) The effect of POSS on the thermal properties of epoxy. Polym Bull (Heidelberg, Germany) 58(5–6):1013–1020

Zhang H-X, Shin Y-J, Yoon K-B, Lee D-H (2009) Preparation and properties of propylene/POSS copolymer with rac-Et(Ind)2ZrCl2 catalyst. Eur Polym J 45(1):40–46

Zhou Z, Zhang Y, Zeng Z, Zhang YJ (2008) Properties of POSS-filled polypropylene: comparison of physical blending and reactive blending. J Appl Polym Sci 110(6): 3745–3751