Synthesis and Properties of Hybrid Urethane Polymers Containing Polyhedral Oligomeric Silsesquioxane Crosslinker

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ABSTRACT: The synthesis and properties of novel hybrid silsesquioxane-containing urethane polymers using octakis(hydroxypropyldimethylsiloxy)octasilsesquioxane (OHPOSS) as a crosslinker and a hydroxyl-terminated polybutadiene were studied. Mixing of the OHPOSS with polyurethane prepolymer and chain extenders in solution was found to be successful when tetrahydrofuran was used as the solvent. Thin films of hybrid polyurethanes were obtained. The hybrid materials were elastomers with improved water and solvent resistivity and good thermal stability. The studied OHPOSS appeared to be an effective crosslinker of polyurethanes suitable for, for example, surface coatings applications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2023–2030, 2013

INTRODUCTION

Polyurethanes (PUs) are a very versatile group of polymers with broad spectrum of applications including cellular materials, adhesives, coatings, elastomers, and so forth. By choosing the appropriate building blocks, the materials of various properties can be obtained. PUs are, in general, synthesized from diisocyanates and polyols, the latter can be of various functionality. In most cases, PUs are used as crosslinked materials. Therefore, the choice of proper crosslinker and appropriate crosslink density is of vital importance.[1]

In recent years, there is a growing interest in the research on organic–inorganic hybrid materials containing polyhedral oligomeric silsesquioxanes (POSS). The reason is the unique cage structure of POSS molecules with nonreactive or reactive organic group R in the cage corners. Nanosized POSS molecules of general formula $(RSiO_{1.5})_n$, where $n = 6–18$, having reactive groups attached to their corners, can either be incorporated to the polymer-chain backbone via covalent bonds,[2,3] or used as an additive, which acts as a nanofiller. Depending on the numbers of the reactive groups, POSS can act in PUs as chain ends or pending side groups (one reactive group), chain extenders (two reactive groups), or crosslinkers (three or more reactive groups).

Partially caged POSS molecules such as trisilanol-POSS[4–8] or tri(hydroxybenzene sulfonic acid)-POSS[9] can be used in the preparation of crosslinked PU hybrid materials. Multifunctional POSS derivatives that have been employed to produce cured PUs have hydroxyl,[10–13] amine,[14–20] or isocyanate[11,21,22] groups.

PU hybrid materials with POSS as crosslinker exhibited greater thermal stability and higher glass transition temperature (T_g),[11,14–18,20,23] hardness,[11,19] and storage modulus.[11,14–16,18] In PU systems, an aggregation of POSS cages,[7,10,15,17] higher hydrophobicity,[7,11,17,19,23] excellent organic solvents, and oxidation resistance[11] were observed. Cured PU materials were used to obtain coatings on metals (steel[4] or aluminum[5,19] substrates), membranes for direct methanol fuel cell applications,[9] and gas permeability membranes[7,17] or shape memory materials.[12,13]

The first synthesis of octa(hydroxypropyldimethylsiloxy)-POSS (OHPOSS) was reported in 2000 by Zhang and Laine.[24] Since then, the OHPOSS has been studied as a component in the synthesis of star poly(ε-caprolactone),[25] polyimide,[26] or was used for the synthesis of other POSS molecules, which were subsequently used for the preparation of poly(methyl methacrylate)-based nanocomposites.[3,27,28] Only two articles reported the application of OHPOSS to the synthesis of PUs.[11,29] In,[11] the hybrid amorphous PU was obtained in a reaction of octakis[m-isopropyl-α,α′-dimethylbenzylisocyanatodimethylsiloxy]octasilsesquioxane and OHPOSS dissolved in tetrahydrofuran (THF). Sakuma et al.[29] synthesized a PU material using the OHPOSS and 2,4-tolylene diisocyanate (TDI)-terminated poly(ethylene adipate) as starting materials.

Hybrid PU/POSS coatings based on hydroxyl-terminated polybutadiene (HTPB)[30] or hydrogenated hydroxyl-terminated polybutadiene (HHTPB)[19] were obtained by the reaction in solution (THF[30] or chloroform[19]). Lai et al.[30] produced hybrid materials

with isophoron diisocyanate, HTPB, and binary chain extender (*trans*-cyclohexanediolheptaisobutyl-POSS and 1,4-butanediol [BD]). These coatings exhibited good corrosion resistance, greater thermal and thermooxidative stability, higher hardness, and T_g. Improved corrosion resistance of aluminum coated with films in which *octa*(*N*-phenylaminopropyl)-POSS was included with poly(hexamethylene diisocyanate) and HHTPB PUs was described by Markevicius et al.[19]

In this study, the syntheses of novel hybrid PU materials using OHPOSS as crosslinker were carried out and their structure, mechanical properties, T_g, solvents uptake, and water contact angle were investigated. The syntheses of PU/POSS hybrid materials were carried out via two-step prepolymer methodology. First, the prepolymer from HTPB and TDI or isophorone diisocyanate (IPDI) was synthesized. This prepolymer was then combined (in solution) with OHPOSS and optionally 1,4-BD (chain extender) to form films. The syntheses of such PU/POSS materials from model diisocyanates or isocyanate-terminated polybutadiene prepolymer, which were crosslinked by OHPOSS, have not been previously reported in the literature.

EXPERIMENTAL

Materials

TDI (a mixture: 80% 2,4- and 20% 2,6-TDI isomers), for synthesis, and IPDI (a mixture of *cis*- and *trans*-isomers), for synthesis, were purchased from Merck Chemicals. 1,4-BD (pure, purchased from Merck Chemicals) was used as received. HTPB (65.0% 1,2-vinyl, 22.5% 1,4-*trans*, and 12.5% 1,4-*cis*), $M_w = {\sim}2000$, $L_{OH} = 51$ mg KOH/g, was purchased from Sartomer. OHPOSS was synthesized as described below. Octakis(hydridodimethylsiloxy)octasilsesquioxane was the product of Hybrid Plastics. Silica-immobilized rhodium siloxide complex was synthesized by Dutkiewicz.[31] Allyl alcohol was purchased from Aldrich. The catalyst used for the syntheses was Kosmos 19 (dibutyltin dilaurate), from Evonik Industries. *N,N*-dimethylformamide (DMF) (pure, from POCH SA) and THF (pure, from Fluka) were dried over molecular sieve prior to use to remove traces of water. Toluene (pure), acetone (pure, from Chempur), and ethyl acetate (pure, from POCH SA) were used as received. The release agent TR-104 (T.R. Industries) was used to facilitate the removal of the samples from the mold.

Synthesis of the OHPOSS

The OHPOSS compound was synthesized in the hydrosilylation reaction in a similar way which is described in our previous article.[22]

Octakis(hydridodimethylsiloxy)octasilsesquioxane (5 g, 4.9 mmol), allyl alcohol with 20% excess (3.5 mL, 51.5 mmol) together with 50 mL of toluene were placed in three-neck, round-bottom flask (100 mL) equipped with magnetic bar, thermometer, and condenser. Next, 102 mg (4.2×10^{-5} mol Rh) of silica-immobilized rhodium siloxide complex (catalyst) was added at a room temperature and the solution was heated to 90°C and kept in this temperature. The reaction was monitored by Fourier-transform infrared (FTIR) spectroscopy and allowed to proceed until Si—H band, at about 2100 cm^{-1}, had disappeared. After 8 h, the reaction mixture was allowed to cool

down and was filtered to remove the catalyst. Toluene and excessive allyl alcohol were then removed under vacuum to yield the product as white solid (6.9 g, 95% of theoretical yield).

The structure of the product was confirmed via FTIR and NMR spectroscopy. FTIR (attenuated total reflectance, ATR): v 3334 (OH), v 2956–2875 (CH), v 1253-900, δ 545 (SiOSi) cm^{-1}; ^{1}H NMR ppm: 0.16 (OSiCH$_3$), 0.61 (SiCH$_2$), 1.63 (CH$_2$), 3.57 (CH$_2$OH), 3.66 (OH); ^{13}C NMR ppm: -0.38 (SiCH$_3$), 13.39 (SiCH$_2$), 26.11 (CH$_2$), 65.03 (CH$_2$OH); ^{29}Si NMR ppm: 13.28 (OSi(CH$_3$)$_2$), -108.96 (SiOSi).

Preliminary Experiments

At first, the solubility of OHPOSS in HTPB polyol, 1,4-BD, TDI–HTPB prepolymer, IPDI–HTPB prepolymer, and THF, ethyl acetate, toluene, DMF solvents was tested. The mixtures of about 2.5 wt % of OHPOSS in the above-mentioned substances were prepared. The solubility was evaluated visually.

Synthesis of Prepolymers

The syntheses of prepolymers were carried out at the molar ratio of diisocyanate : polydiol of 2.1 : 1 ($I_{NCO} = 1.05$) in a flask under nitrogen mantle at 80°C for 1 h, followed by 3 h at 100°C. The reaction mixture was stirred mechanically. After 2 h of synthesis, 0.06 wt % of Kosmos 19 catalyst was added to the mixture.

Preparation of Cured PU/POSS Films

A matrix of PU/POSS films was obtained as summarized in Table I. The appropriate amount of OHPOSS was dissolved in 3 mL of THF. In case of the films containing a chain extender, 1,4-BD was added to the previously prepared solution of OHPOSS in THF. The calculated amount of prepolymers or diisocyanate was added to the THF solution while stirring vigorously. When the clear solution was obtained, 1 wt % of Kosmos 19 catalyst was added (with continuous stirring). The reactive mixtures were poured onto flat PET sheet (coated with the release agent), which was placed in a glass horizontal mold. The THF solvent was allowed to evaporate, resulting in films cast on the release agent-coated PET film. The dry film samples were allowed to cure at room temperature in air for 7 days. The cured samples of hybrid PU/POSS were then removed from the mold and tested.

Characterization of Materials

Analysis of Chemical Structure. FTIR spectra of OHPOSS were obtained using a Bruker Tensor 27 apparatus (Bruker Optik GmbH, Germany) equipped with a SPECAC Golden Gate diamond ATR accessory. ^{1}H NMR (300 MHz), ^{13}C NMR (75.5 MHz), and ^{29}Si NMR (59.6 MHz) spectra of OHPOSS were recorded on a Varian XL 300 spectrometer at room temperature (298 K) using CDCl$_3$ as solvent.

FTIR spectra of the prepolymers and hybrid materials were obtained using a Nexus Nicolet 5700 (Thermo Fisher Scientific, USA) apparatus. The samples of prepolymers were cast from THF solutions onto KBr disks. The cured films of about 0.25 mm thickness were tested as self-supporting samples in holders.

Tensile Measurements. The tensile measurements were performed on stripes of 70 $\times$ 15 $\times$ 0.25 mm, which were cut

Table I. The Percentage Composition and Hard Segment Content in Polyurethane Hybrid Materials

Sample designation	Hard segment content (wt %)	Composition (wt %)					
		OHPOSS	BD	IPDI–HTPB	TDI–HTPB	IPDI	TDI
PU TDI-HTPB + OHPOSS + BD (1 : 7)	5.06	1.87	3.19	–	94.94	–	–
PU TDI-HTPB + OHPOSS + BD (1 : 3)	6.39	3.69	2.70	–	93.61	–	–
PU TDI-HTPB + OHPOSS + BD (1 : 1)	8.93	7.18	1.75	–	91.07	–	–
PU TDI-HTPB + OHPOSS	13.63	13.63	–	–	86.37	–	–
PU TDI-HTPB + 150% OHPOSS	19.14	19.14	–	–	80.86	–	–
PU IPDI-HTPB + OHPOSS + BD (1 : 7)	4.88	1.81	3.07	95.12	–	–	–
PU IPDI-HTPB + OHPOSS + BD (1 : 3)	6.16	3.56	2.60	93.84	–	–	–
PU IPDI-HTPB + OHPOSS + BD (1 : 1)	8.61	6.93	1.68	91.39	–	–	–
PU IPDI-HTPB + OHPOSS	13.17	13.17	–	86.83	–	–	–
PU IPDI-HTPB + 150% OHPOSS	18.53	18.53	–	81.47	–	–	–
PU TDI + OHPOSS	100.00	68.03	–	–	–	–	31.97
PU IPDI + OHPOSS	100.00	62.51	–	–	–	37.49	–

from the resulted cured films. The mechanical properties were investigated at room temperature (25°C). The tensile data were obtained on universal testing machine Zwick/Roell Z020 (Zwick GmbH & Co. KG, Germany) at a crosshead speed of 10 mm/min and gauge length of 30 mm. The average of three measurements of tensile strength, elasticity modulus (Young's modulus), and ultimate elongation was calculated from the tensile data by controlling software of the testing machine.

Thermal Properties. T_g were measured on a Pyris 6 differential scanning calorimeter (DSC) (Perkin Elmer, USA) under N_2 at 10°C/min heating rate and temperature range from −70 to 160°C. T_g was determined from the second run of measurement.

Contact Angle Measurements. Contact angle measurements were carried out at 22°C using double-distilled water as wetting medium. The tests were performed on Tracker H instrument (Teclis, France). The drop of water from the microsyringe was placed on the PU/POSS film on the opposite side to mold surface (free of release agent). The contact angle was measured automatically after placing a drop on the sample. The results are calculated as the average of three measurements taken after 240 s.

Solvent Uptake Measurements. Hybrid PU/POSS films of dimensions 15 × 15 × 0.25 mm were placed in a polypropylene containers with 10 mL of solvent (distilled water, acetone, or toluene). The mass of samples was measured at room temperature (25°C) after 1, 4, 7, and 14 days. The films were dried with filter paper before each weighting. The percentage solvent uptake (U) was calculated from the following equation:

$$U = \frac{m_z - m_s}{m_s} \times 100$$

where m_z is the mass of sample with absorbed solvent and m_s is the mass of dry sample.

RESULTS AND DISCUSSION

Synthesis and FTIR Spectra Analysis of the PU/POSS Hybrid Materials

The OHPOSS solubility tests were carried out to show whether it is possible to use OHPOSS in bulk PU syntheses. The synthesis in bulk requires all reagents (polyol, isocyanate, crosslinker, and chain extender) to be soluble in each other.[22] However, the tested OHPOSS appeared to be insoluble or only partly soluble at normal temperature in the tested polyols and prepolymers. Therefore, we found that the bulk synthesis of PU/POSS from these reagents is impossible. OHPOSS was found to be fully soluble in THF and DMF solvents, which were also good solvents of the remaining reagents. We choose THF as the solvent to further synthesis owing to its higher volatility.

In further tests, the so-called prepolymer method of PU/POSS syntheses was used. The reason was a higher repeatability of structure and higher structural order of the obtained PU/POSS (Figure 1). This is contrary to the so-called "one-shot" method, in which all reagents are mixed simultaneously and react at a rate, which is dependent on their relative reactivity and mobility in highly viscous reaction medium. In a reaction of our interest, there are three kinds of OH groups—the ones in HTPB, BD, and OHPOSS—which compete in reacting with NCO groups of diisocyanate used.

To check the reactivity of OHPOSS against the diisocyanates, we have carried the reaction of TDI or IPDI with OHPOSS in THF. The stoichiometric ratio of OH : NCO groups in both reagents was maintained. As a result, the films of properties summarized in Table II were obtained. The reaction catalyzed by 1 wt % of Kosmos 19 was fast and exothermic. The analysis of FTIR spectra revealed the presence of urethane link (N—H bending at 3290 cm^{-1}, N—H stretching at 1540 cm^{-1}, C=O stretching at 1733 cm^{-1}). A peak centered around 2265–2274
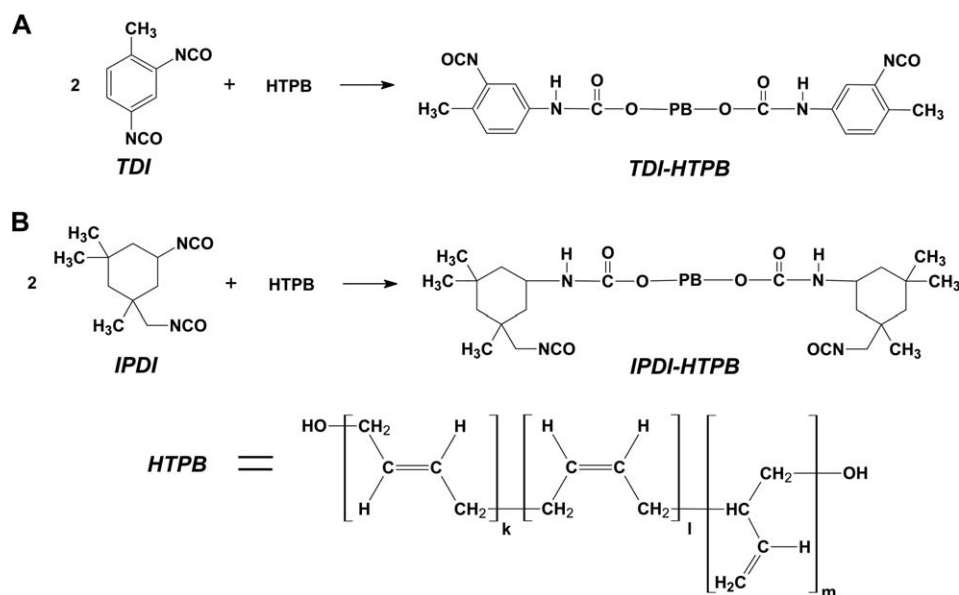
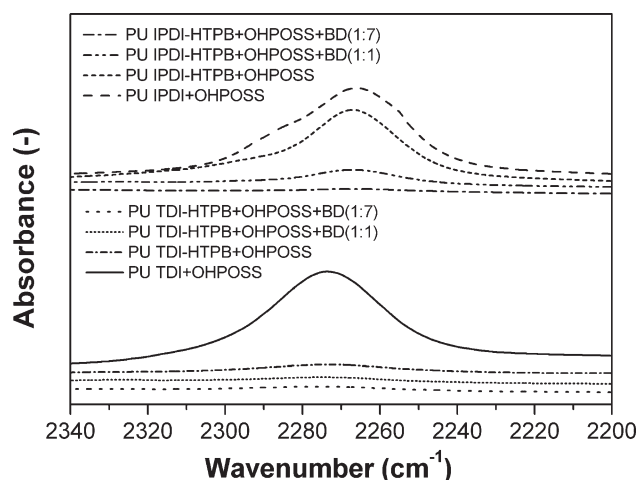**Figure 1.** Syntheses of (A) TDI–HTPB and (B) IPDI–HTPB prepolymer.

Table II. Mechanical Properties and Solvent Uptake of OHPOSS-cured Polyurethanes

Sample designation	Young's modulus E_t (MPa)	Ultimate elongation ε (%)	Tensile strength σ_M (MPa)	Uptake U (%)		
				Water	Acetone	Toluene
PU TDI + OHPOSS	614 ± 29	2.4 ± 0.7	18.1 ± 3.7	1.40	15.93	9.42
PU IPDI + OHPOSS	427 ± 31	35.5 ± 22.9	21.0 ± 2.8	0.73	18.18	18.37

cm^{-1} (N═C═O stretching) shows the incomplete reaction of NCO groups (Figure 2). This is not surprising in so highly crosslinked systems with reduced mobility of OH groups linked to a rigid POSS cage in the final step of reaction.

The synthesis of prepolymers is shown in Figure 1. The structure of prepolymers was confirmed by FTIR spectra (Figure 3). Several syntheses of hybrid PU/POSS materials were carried out

by the above-described method. Variable OHPOSS : BD ratios were used, resulting in hybrid PUs of various crosslink densities. The structures of the PU/POSS obtained are shown in Figure 4. The amount of reagents for syntheses and their ratios are listed in Table I. The FTIR spectra revealed higher reactivity of TDI–HTPB prepolymer toward OH groups, as compared to the IPDI–HTPB prepolymer (Figure 2). The films produced from the latter prepolymer show a small peak of NCO (at 2267 cm^{-1}), whereas those from TDI–HTPB did not.

Mechanical and Thermal Properties
The mechanical properties of the PU/POSS hybrid materials are shown in Table II and Figures 5–7. The obtained polymers are of elastomeric character. The only exception are samples produced in direct synthesis from diisocyanates and OHPOSS as only reagents, which are hard solids with properties summarized in Table II.

As shown in Figures 5–7, it may be seen that the increase of POSS content in the studied PUs results in Young's modulus (E_t) increase,[8,18,23] lowering of ultimate elongation (ε), but also in unexpected decrease of tensile strength (σ_M). The mechanical properties of derived hybrid materials are mainly dependent on the degree of crosslinking (E_t and elongation) and the degree of order PU structure (σ_M). The introduction of OHPOSS has increased the stiffness of the material as a result of higher
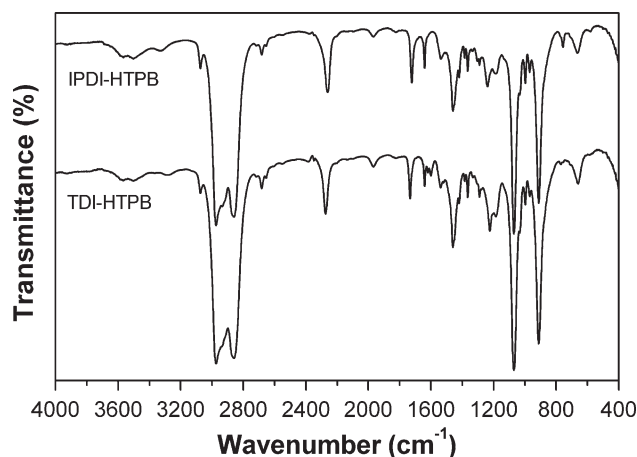

Figure 2. FTIR spectra of the NCO stretching region in PUs.

Figure 3. FTIR spectra of prepolymer.

degree of crosslinking (increased E_t and decreased ε). When the content of OHPOSS-derivative in IPDI–HTPB-based PU was <3.7 wt %, it was found that tensile strength increased. However, an observed decrease in σ_M at higher OHPOSS content may be owing to the increased disorder and hindered phase separation of hard and soft PU segment. It may be the fact that during the formation of a crosslinked hybrid material with higher OHPOSS content the mobility of reactive species is gradually reduced. This may cause the incomplete conversion of monomers.[32,33] This is particularly visible for PUs based on IPDI–HTPB (Figure 2).

The results of the measurements of thermal properties are shown in Figures 8 and 9. DSC thermograms show no significant changes for cast (first run) and annealed hybrid materials (second run). In the first run, the residual solvent was completely removed, as well as thermal history of the material was cancelled (Figure 9). The T_g for PU soft segment was observed only in the second run of DSC measurement. The other T_g for the PU hard segments and the OHPOSS clusters were not visible in DSC diagrams. The obtained values of T_g are characteristic for elastomers and are in the region of $-35°C$. The values of T_g are only slightly dependent on POSS content. This is not surprising as T_g is a value measured for soft PU segment to which POSS does not contribute.

Solvent Uptake and Water Contact Angle Measurements

Three solvents were used for this experiment—water, slightly polar acetone, and nonpolar toluene. The results are shown in Figures 10–13 and in Table II. The absorption of solvents by all derived hybrid materials is only slightly dependent on immersion time and uptake equilibrium is reached after 7 days. The solvent uptake of exemplary PUs (TDI–HTPB + 150% OHPOSS and IPDI–HTPB + 150% OHPOSS) as a function of immersion time is shown in Figure 10. The absorption of water by the PUs under study is low and only slightly dependent on POSS content. The absorption of acetone is considerably higher (30–35 wt %), but decreases with the increasing content of POSS (higher degree of crosslinking), but rises again when the stoichiometric content is overrun. This is probably owing to the presence of unreacted OH groups, which raise the polarity of the polymer. The sorption of toluene is high at lower POSS content, but decreases as the crosslink density is larger owing to higher POSS content in samples. It is worth noting that all samples retained their integrity even at the highest toluene uptake—no solvent cracking is observed.
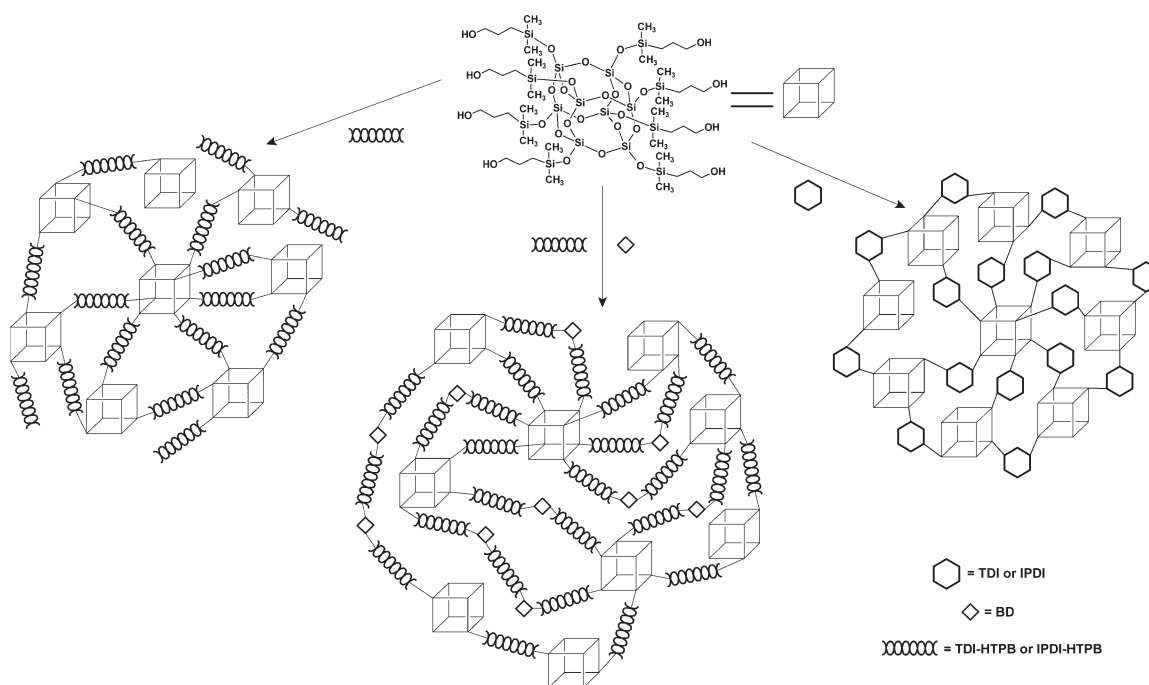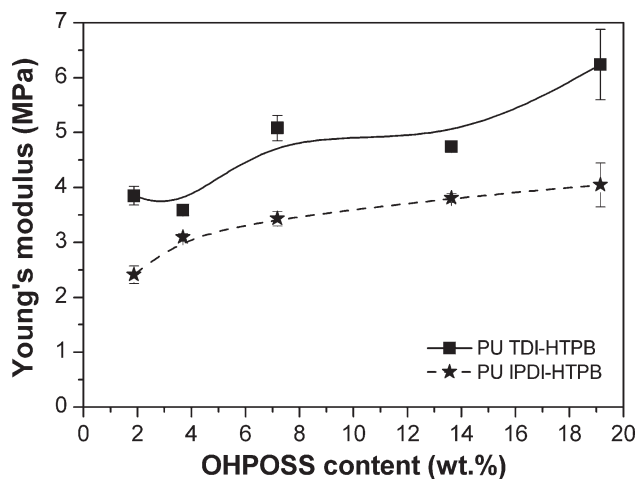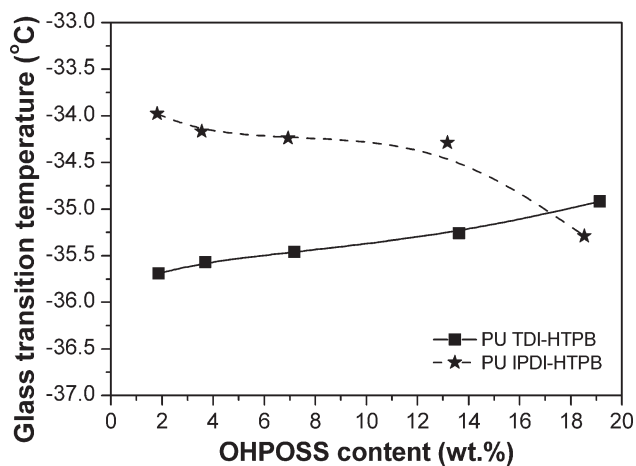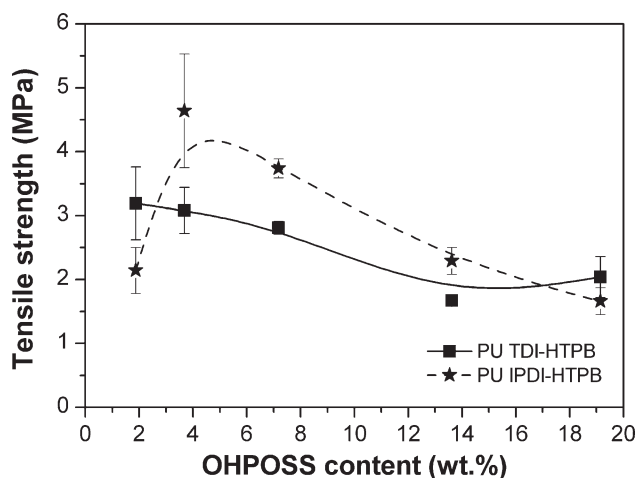

Figure 4. Structures of PU/POSS hybrid materials.
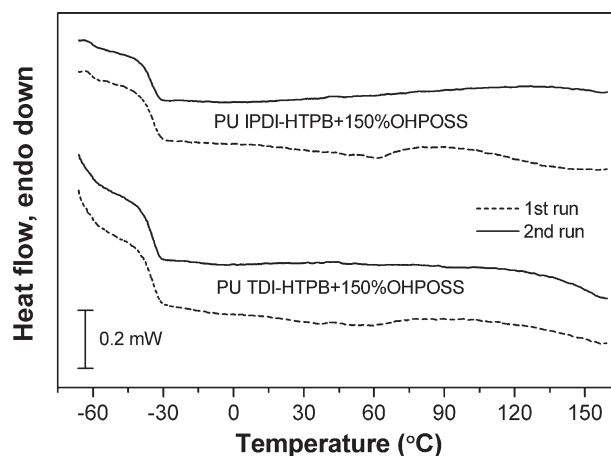
Figure 5. Young's modulus of TDI–HTPB-based and IPDI–HTPB-based hybrid materials as a function of OHPOSS content.
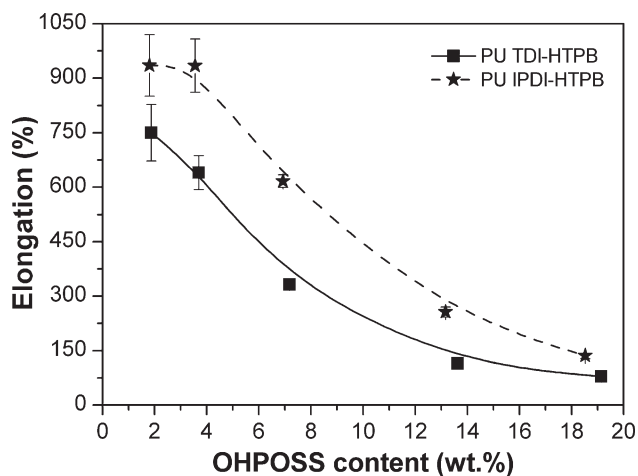

Figure 8. T_g of TDI–HTPB-based and IPDI–HTPB-based hybrid materials as a function of OHPOSS content.
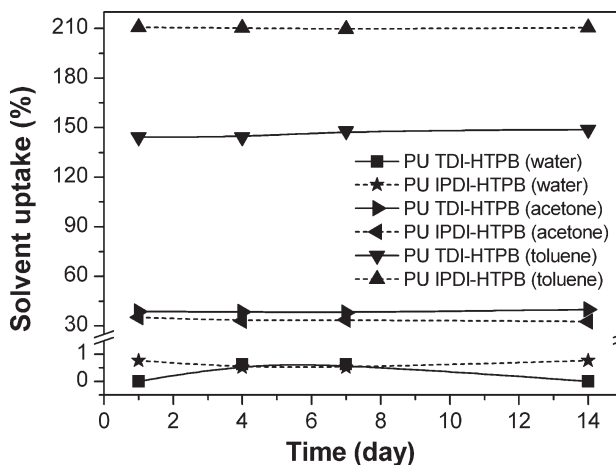

Figure 6. Tensile strength of TDI–HTPB-based and IPDI–HTPB-based hybrid materials as a function of OHPOSS content.
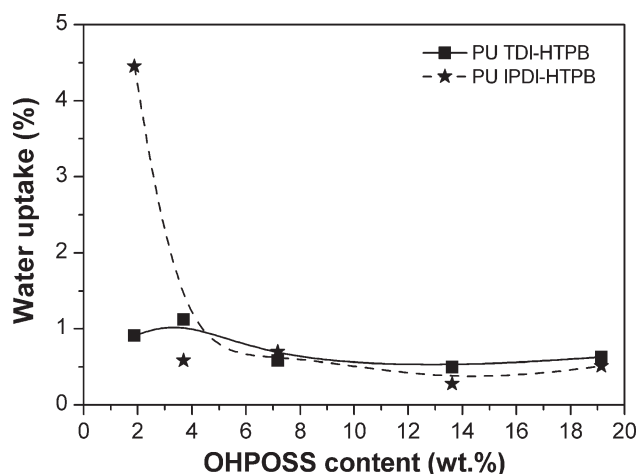

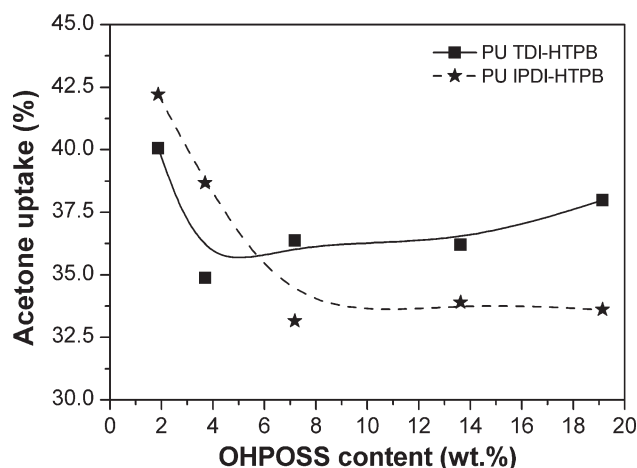**Figure 9.** DSC thermograms of exemplary hybrid materials.

Figure 7. Ultimate elongation of TDI–HTPB-based and IPDI–HTPB-based hybrid materials as a function of OHPOSS content.


Figure 10. Solvent uptake of TDI–HTPB + 150% OHPOSS and IPDI–HTPB + 150% OHPOSS hybrid materials as a function of immersion time.
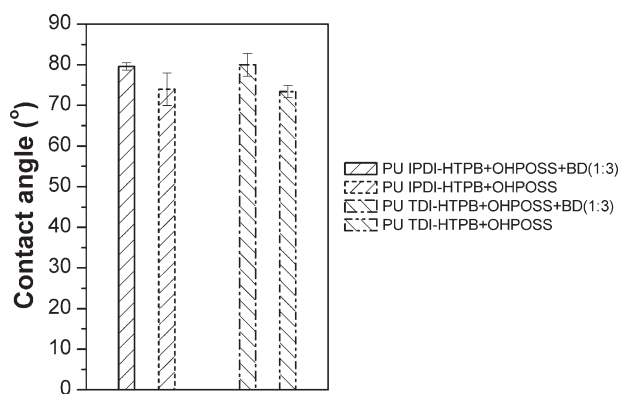
Figure 11. Water uptake of TDI–HTPB-based and IPDI–HTPB-based hybrid materials after 7 days of immersion as a function of OHPOSS content.

Figure 14. Water contact angle of exemplary hybrid materials for 240 s.

The sorption of toluene has also been found to depend on isocyanate type. The cycloaliphatic IPDI produces PUs of higher toluene sorption ability than that of PU samples produced from aromatic TDI. This may be owing to the higher stiffness of aromatic rings containing PUs. This also correlates well with the values of Young's modulus as shown in Figure 5.

The contact angle measurements (Figure 14) did not show the positive effect of POSS content on hydrophobicity of hybrid materials under study. This may be owing to the fact that POSS cages are located mainly inside the PU structure and do not contribute to the surface properties of the PUs. Moreover, the unreacted hydroxyl groups increase the hydrophilicity of the hybrid materials.

CONCLUSIONS

The OHPOSS under study has been found to be an effective crosslinker for PU elastomers. The obtained hybrid PUs were elastomers with improved water, solvent resistivity, and good thermal stability. Owing to poor solubility of OHPOSS in reagents for PU synthesis (polyols, prepolymers, and chain extenders), it is unsuitable for syntheses to be carried out in bulk, but may be useful in solvent-based compositions, for example in surface coating applications.

Figure 12. Acetone uptake of TDI–HTPB-based and IPDI–HTPB-based hybrid materials after 7 days of immersion as a function of OHPOSS content.
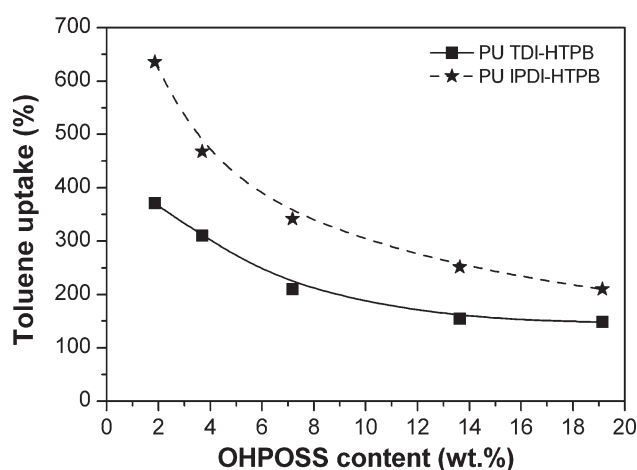
Figure 13. Toluene uptake of TDI–HTPB-based and IPDI–HTPB-based hybrid materials after 7 days of immersion as a function of OHPOSS content.

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