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Phenylsilane; unreactive group in the metallocene/MAO catalyzed copolymerization of propylene and 7-octenyldimethylphenylsilane, reactive group in melt blending with microsilica filler

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ABSTRACT

In this study, 7-octenyldimethylphenylsilane (7-SiPh) was copolymerized with propylene using $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-1-indenyl})_2\text{ZrCl}_2/\text{MAO}$ as a catalyst. The copolymerization behaviour of the silicon-containing monomer, 7-SiPh, was compared with that of 1-dodecene, which is known to be incorporated in polypropylene (PP) using metallocenes. Both comonomers were well incorporated and randomly distributed in the main chain and had no marked influence either on the tacticity or the molar mass of the PP. In the next step, the reactivity of the synthesised polypropylene-co-octenyldimethylphenylsilane (PP-co-SiPh) was increased by post-treatment with HBF_4 to give the highly reactive fluorosilane form (PP-co-SiF). The reactivities of the post-treated form, PP-co-SiF, as well of the untreated copolymer, PP-co-SiPh, were tested by using them as modifiers (0.1–0.4 phr) in composites of commercial polypropylene and microsilica (μSi 1–4 phr). When PP-co-SiF was the modifier the influence on the morphology of the composite was negligible. However, the crystallization temperature of the PP matrix was found to increase $>8^\circ\text{C}$ at most, indicating an increased adsorption of the polymer on the filler surface. Most interestingly, the untreated PP-co-SiPh showed almost the same influence on the properties of the composites, indicating an interaction/reactivity between the (hexyl)dimethylphenylsilane side group and the microsilica filler. The suspected reactivity was separately confirmed by successful coating of microsilica filler with molecular trimethylphenylsilane. The phenylsilane was found to react in a manner similar to how the halosilanes react with the hydroxyl groups at the silica surface. To our knowledge, this reaction is reported for the first time.

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1. Introduction

The addition of mineral fillers into thermoplastics serves several purposes besides that commonly known cost savings. With a proper filler choice we can influence e.g. the stiffness, the dielectric loss and the absorption of infrared radiation of the composites. Polypropylene is the one of the most commercially important filled polymers and is widely used in many fields of applications. New initiatives on recycling, particularly in automotive industry,

are tending to limit polymer types used. The environmental friendly polypropylene is strongly favoured and this helps to drive the market for filled grades [1–3].

One of the major problems in filler/polyolefin composites is that the hydrophilic mineral fillers tend to form aggregates, mainly due to the strong filler/filler interaction. The interaction of the hydrophilic fillers is often reduced through coating with long chain aliphatic carboxylic acids (e.g. stearic acid) which makes the filler surface hydrophobic. However, to achieve all the benefits offered by the filler, also the filler/matrix interaction must be controlled [2,4]. The reactivity of polyolefins towards fillers can be enhanced by adding functional groups to the polyolefin chain. The functional groups react with the filler, helping

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the filler to be well bonded to the matrix and, in some cases, also to disperse the filler more homogeneously in the matrix [5–9].

While the copolymerization of olefins with functional monomers has been successfully utilized in high pressure free radical processes (>2500 bar, >300 °C), controlled copolymerization of functional monomers under mild conditions with coordination catalysts still remain as a challenging task. A widely studied area in the functionalization of polyolefins has been the metallocene catalyzed copolymerization of olefins with polar comonomers containing a heteroatom [10–17]. However, the activity of the catalyst usually decreases rapidly as the lone electron pair of the heteroatom co-ordinates to the active center. Also, the molar mass of the final polymer is often reduced markedly when a polar comonomer is used. Other approaches towards functionalization of polyolefins are to use polar/reactive comonomers that do not have heteroatoms with free electrons (so-called weakly interacting monomers e.g. dienes, *p*-methylstyrene, comonomers containing alkylborates or a phenylsilane as functional group) [17–25]. Such comonomers do not usually deactivate the metallocene catalyst, nor do they influence the molar mass of the polymer. As a drawback, these weakly interacting polyolefins require a separate post-treatment step before they are reactive enough to be used as modifiers in polyolefin based composites.

In this study, copolymerization of propylene with a weakly interacting silane comonomer (7-octenyldimethylphenylsilane) was examined. In addition, the synthesised copolymer, PP-co-SiPh, was post-treated to produce its more reactive analogue, PP-co-SiF. (Fig. 1) These two copolymers were then tested as modifiers in composite of microsilica (μ Si) and polypropylene, and their influence on mechanical, thermal, and morphological properties of the composite were studied. Surprisingly, also the untreated PP-co-SiPh influenced strongly on the composite and therefore the interaction between (hexyl)dimethylphenylsilane side group and microsilica filler was studied in more detail. Finally, the reaction between (trimethyl)phenylsilane and hydroxyl groups on the microsilica surface was confirmed.

2. Experimental

2.1. Materials

The catalyst, *rac*-dimethylsilylbis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride ($(\text{CH}_3)_2\text{Si}(2\text{-Me-4-Ph-Ind})_2$ -

ZrCl_2) was obtained from Boulder Scientific company, and the cocatalyst, methylaluminoxane (MAO 10 wt-% in toluene), was obtained from Witco GmbH and they were used as received. Propylene (Messer, grade 3.5) and toluene (Merck KGaA, pro analysis), were purified by passing them sequentially through a molecular sieve column, an Al_2O_3 column, and then a CuO column. 1-Dodecene, used as a comonomer, was purchased from Aldrich (>95%) and dried by molecular sieves before use. 7-Octenyldimethylphenylsilane was produced as described previously [25]. After synthesis the copolymer (PP-co-SiPh) was treated with HBF_4 (54 wt-% in diethyl ether) from Aldrich. The polypropylene, HE125MO (MFR 12 g/10 min, 230 °C/2.16 kg, no nucleating agents), was supplied by Borealis Polymers Oy. The commercial grade modifier used as a reference was PolyBond 1002 (PP-g-COOH, acrylic acid 6 wt-%) from Uniroyal Chemicals. Amorphous uncoated microsilica was from Elkem Materials, grade MS 983, with an average spherical particle size of 0.15 μm , density of 2.2–2.3 g/cm^3 and specific surface area of 15–30 m^2/g . Phenyltrimethylsilane (Petrarch Systems, b.p. 169 °C) and chlorotrimethylsilane (Fluka, >99.0%) were used as coating agents on microsilica.

2.2. Polymerization

Polymerization reactions were carried out in a 0.5 dm^3 stainless steel Büchi autoclave equipped with a propeller-like stirrer. After careful evacuation of the reactor, the polymerization medium (toluene) and MAO were introduced under vacuum. The reactor was filled with nitrogen to ambient pressure and the comonomer was fed to the reactor. Finally, the propylene pressure was adjusted and after it had reached equilibrium, the catalyst was fed to the reactor. The propylene concentration in the polymerization medium was kept constant during the polymerization by continuous feeding and vigorous stirring. The progress of polymerization was followed using a mass-flow meter to monitor propylene consumption. Compared to the homopolymerization of propylene, the catalyst activities were lower in copolymerizations, and to reach a significant amount of copolymer longer polymerization times were needed. The catalyst activities remained stable throughout the polymerizations and the variations in times (10–45 min) did not notably influence the calculated catalyst activities. Polymerizations were stopped by degassing the reactor, and pouring the reaction mixture into an HCl/ethanol solution. After stirring (~ 3 h), the polymer was filtered out, washed with ethanol, filtered again, and dried.

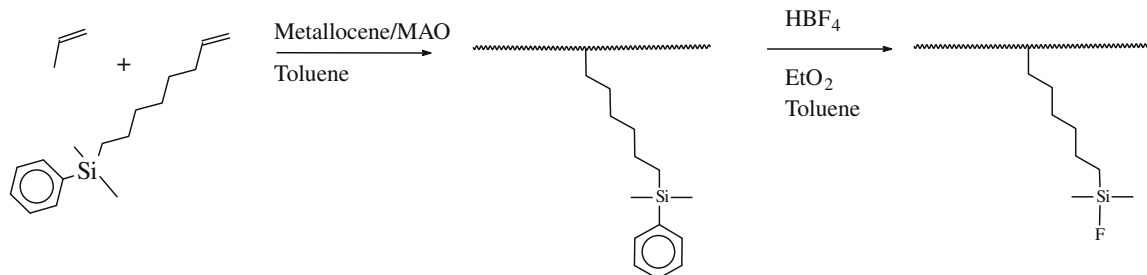


Fig. 1. Route to fluorosilane functionalized polypropylene.

2.3. Post-treatment

The protodesilylation was carried out mainly as previously described [25]. Two grams of the copolymer (PP-co-SiPh) was placed in a 100 ml three-necked round bottom flask with a condenser under an argon atmosphere and dissolved in 40 ml of hot toluene (100–105 °C). About 10–15 equivalents of the post-treatment reagent (HBF_4 in diethyl-ether) was added slowly through a valve and the reaction was allowed to continue for 4 h. The solution was allowed to cool, after which it was precipitated in ethanol. After filtration (and drying), the residue was purified to remove the silicates dissolved from the glass reaction vessel due to reaction with HF in the reagent. The residue was extracted in hot toluene, allowed to cool, precipitated in ethanol, filtered, and dried.

2.4. Preparation of composites

Polypropylene (HE125MO) and uncoated microsilica (μSi) were premixed (70/30 wt-%) by melt blending in a co-rotating Brabender Plasti-Corder PLE 651 with DSK 42/7 twin-screw extruder. The blending temperature was 210 °C and the screw speed 60 rpm (mean delay time of the extrudate 250 s.). The final composites (μSi 1, 2, and 4 phr) were prepared in a twin-screw midiextruder ($T = 220$ °C, DSM, speed 75 rpm, capacity 16 cm³, length 150 mm) by blending pure polypropylene, the pelletized premixed PP/ μSi -extrudate and polypropylene based functional modifier (0.1–0.4 phr). After mixing for 5 min the blend was injection molded into tensile test specimens. The mold temperature was 40 °C.

2.5. Coating of microsilica

The coating agents were reacted with the microsilica surface by vapor deposition in a closed cell. One gram of microsilica and 1 mmol of coating agent (~ 0.15 – 0.2 ml) were placed separately in a 0.1 dm³ metal cell under argon atmosphere. The cell was closed tightly and moved on a heated oil bath where the reaction was controlled by time and temperature. During reaction, the overpressure in the cell settled at 0.5–0.8 bar. After reaction, the microsilica was dried in vacuum at 200 °C for 24 h and its surface was characterized by DRIFT. The reagent residues from the bottom of the cell were characterized by ¹³C NMR.

2.6. Characterization

The molar masses (M_w) and molar mass distributions (PD) were determined with a Waters Alliance GPCV 2000 gel permeation chromatograph equipped with four Waters Styragel columns (HMW 7, 2 × HMW 6, HMW 2) and a refractive index detector. 1,2,4-trichlorobenzene was used as a solvent at 140 °C and applied at a flow rate of 1.0 ml/min. Narrow molar mass distribution polystyrene standards were used for calibration of the columns.

The degree of comonomer conversion during copolymerization as well the microstructure of the polymer were determined from ¹³C NMR and DEPT spectra run with a Varian Gemini 2000 300-MHz NMR spectrometer. The

copolymers were dissolved in 1,2,4-trichlorobenzene containing 10 vol-% of benzene-d₆ and the NMR spectra were recorded at 125 °C. As an internal standard, the methyl *mmmm* pentad resonance peak of polypropylene was placed at δ 21.800 ppm in the ¹³C NMR spectrum. To analyze the conversion of the post-treatment reaction the sample was dissolved in C₂D₂Cl₄ and the ¹H NMR spectra were recorded at 110 °C. As an internal standard the C₂HDCl₄ residue resonance peak was placed at δ 5.9 ppm.

The melting temperatures and enthalpies of polymers were measured with a Mettler Toledo DSC 821^e differential scanning calorimeter under a nitrogen atmosphere. To achieve better contact between the sample and the aluminum sample pan, the sample (pure polymer 5.5 ± 0.5 mg; composite 7.5 ± 0.5 mg) was pre-melted in the pan (on a hot plate, 180 °C) at the same time as it was pressed firmly on the bottom of the pan. Before non-isothermal runs the thermal history of the polypropylene was destroyed by heating the sample to 220 °C at 20 °C/min and holding it there for 1 min. The crystallization behaviour was then determined from the peak area and the peak temperature of the crystallization exotherm (T_c), obtained at a cooling rate of 10 °C/min (from 220 °C to 0 °C). After the cooling step, the melting endotherms (ΔH) and the peak melting temperatures (T_m) were measured by reheating the sample at 10 °C/min.

The tests of tensile properties were carried out with an Instron 4204 universal testing machine according to the standard ISO 527-1993(E) with the specimen type 1BA. The test speed was 1 mm/min and modulus, yield strain, and yield strength were recorded. Tensile strength and strain were not measured due to the high straining of the sample (>1300%) at which point the sample also started to strain between the grip gauges. Before tensile testing, the samples were conditioned for at least 72 h at 23 °C and 50% relative humidity.

The microsilica dispersion in polypropylene matrix was estimated with Olympus BH2 optical microscope equipped with a digital camera. Samples for microscopy were cut from the tensile test specimen (cross sectional area of 10 × 1.5 mm) using microtome (Microm HS325). The sample thickness was 40 μm and it was placed between two glass plates. To optimize the contrast between the polypropylene matrix and the microsilica aggregates the samples were melted between the plates followed by rapid quenching in liquid nitrogen. The concentration of microsilica aggregates was estimated by calculating the cross-cut area of the visible aggregates using ImageJ 1.40 g software.

The surface of the microsilica filler was characterized using Nicolet Nexus FTIR-spectrometer. DRIFT-spectra were acquired using 128 co-added scans at 4 cm⁻¹ resolution.

3. Results

3.1. Polymer synthesis

3.1.1. Characterization of polymers

The microstructures of the synthesised PP-co-SiPh were determined based on the ¹³C NMR (Fig. 2A) and DEPT (Fig. 2A, inset 1) spectra. In addition to the three main peaks from the primary, secondary and tertiary carbons

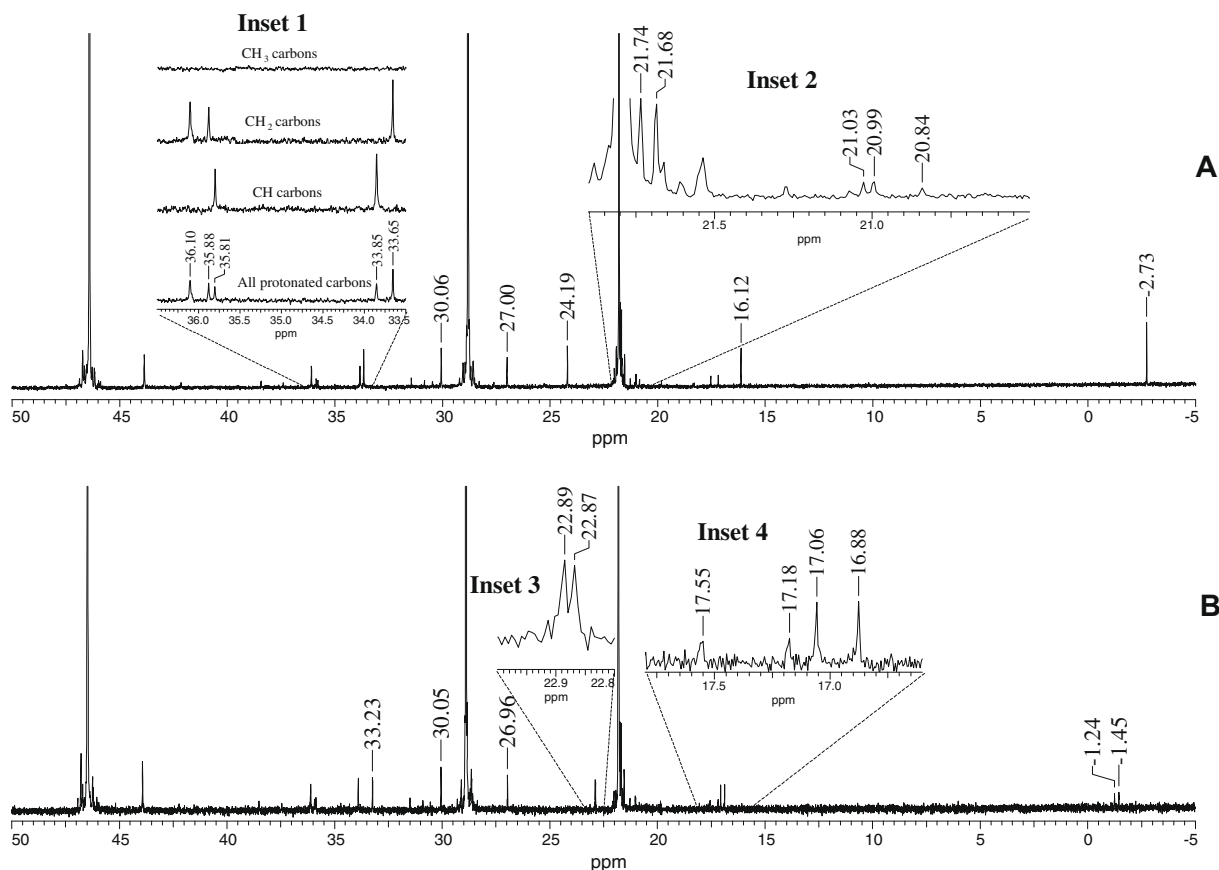


Fig. 2. (A) ^{13}C NMR and ^{13}C DEPT (inset 1) spectra of the polymer PP 3, and (B) the ^{13}C NMR spectrum of PP 3 after conversion of phenylsilane groups to fluoro-silanes (PP 3 F) by post-treatment.

of the main chain, several peaks were observed due to side chains formed by comonomer insertion. The ^{13}C NMR shifts due to the carbons near the branching point were assigned (Table 1) by comparing the spectrum with the known peak positions of the comparable polyethylene-based copolymer [25] and of the propylene/ α -olefin copolymers [26,27]. The separation between the C4 and the branching carbon (br) was verified by ^{13}C DEPT analysis (Fig. 2A, inset 1).

In addition to the shifts assigned by these references, we also observed shifts (at ~ 21.68 , ~ 21.74 , ~ 28.78 , ~ 28.90 and 46.75 ppm) with intensities that increased with the concentration of the incorporated comonomer. It was clearly that these shifts originated from carbons near the branching point in the main chain. However, the exact correlation between these shifts vs. carbons in main chain was not possible to determine. The shift at ~ 46.75 ppm was from a secondary carbon and it likely originated from the carbon at the γ -position counted from the branching carbon. The shifts at 21.68 and 21.74 ppm (Fig. 2A, inset 2) originated from methylene carbons at the P1 and P2 positions. The tertiary carbon shifts, at 28.78 and 28.90 , most likely originated from the carbons at β - and δ -positions.

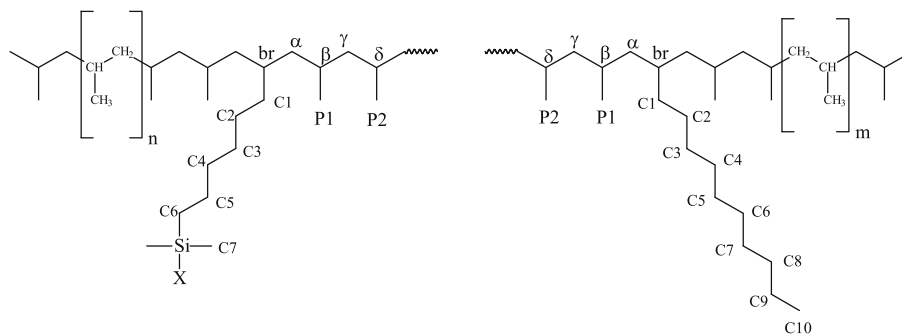
In addition to the shifts from the comonomer insertion, the rest of the peaks in the ^{13}C NMR spectra were due to

2,1 and 3,1 misinsertions (or four isolated methylene units) of propylene, *mmrr* and *mrrm* pentad methyl sequences, as well traces of *i*-butyl end groups. The presence of all these segments in the polypropylene resulted in multiple small shifts, especially around 21 ppm (Fig. 2A, inset 2, 21.09, 21.03, 20.99, 20.84 ppm), complicating the peak assignment. The shifts were verified mainly based on earlier results from our laboratory though the precise numerical values of the shifts were not reported there [28]. The peak assignment was confirmed with the ^{13}C DEPT experiments and precise shifts are presented in Table 2. The DEPT was especially useful for separating the shifts from C2 and C7 carbons in the sequence formed after 2,1 misinsertion (Table 2, Fig. 2A, inset 1).

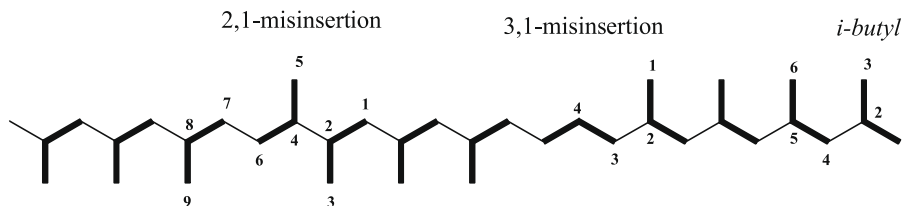
The presence of *i*-butyl end groups alone indicates that the chain transfer to aluminium was the dominating chain termination reaction. The methyl shifts from *mmrr* and *mrrm* pentad sequences (at 20.99 and 19.84 ppm, respectively) were observed at a ratio of 2:1, indicating enantiomeric-site control in propylene insertion [29]. The methyl shift from the *mmmr* pentad (at ~ 21.54 ppm) was overlapped by a spinning side band.

3.1.2. Polymerizations

The polymerization of propylene with a similar kind of catalyst system was described in an earlier study [28].

Table 1Observed ^{13}C NMR shifts due to side chains formed by comonomer insertion in the polypropylene chain.

Carbon		Shift in ^{13}C NMR spectra ppm (± 0.02 ppm)	
Main chain			
CH ₃		21.800	
CH ₂		46.44	
CH		28.85	
br		33.85	
α		43.89	
$\beta + \delta$		28.78 + 28.90	
γ		46.75	
P1 + P2		21.68 + 21.74	
Side chain	X = Ph	X = F	1-Dodecene (side chain C10)
C1	36.10	36.09	36.10
C2	27.00	26.96	27.11
C3	30.06	30.05	30.47
C4	33.65	33.23	28.89–28.96
C5	24.19	22.88	28.89–28.96
C6	16.12	Doublet, $J = 1.4$ Hz 16.97	28.89–28.96
C7	-2.73	Doublet, $J = 13$ Hz -1.35	29.55
C8	-	Doublet, $J = 16$ Hz	32.15
C9	-	-	22.84
C10	-	-	14.06

Table 2Observed ^{13}C NMR shifts due to misinsertions and end groups in the polypropylene.

Shift in ^{13}C NMR spectra ppm (± 0.02 ppm)			
Carbon	2,1 misinsertion	3,1 misinsertion	<i>i</i> -butyl end group
C1	42.18	20.84	22.54
C2	35.81	30.87	25.84
C3	17.55	37.42	23.77
C4	38.46	27.62	47.52
C5	17.18	-	-
C6	30.51	-	21.09
C7	35.88	-	-
C8	31.46	-	-
C9	21.03	-	-

Table 3

Properties of the polymerization products.

Run	Propyl. in feed (mM)	Comon. in		Catalyst activity (kg/mol bar h)	$M_w \cdot 10^{-3}$ (g/mol)	PD	Regio + stereo defects			Thermal properties		
		feed (mM)	polym. (mol-%)				2,1-ins. (%)	3,1-ins. (%)	<i>mrrm</i> (%)	T_m (°C)	T_c (°C)	ΔH (J/g)
PP 1	205	–	–	317,000	91	1.9	0.29	0.09	0.20	153.4	113.7	95
PP 2	205	7.1	0.66	160,000	91	1.9	0.28	0.08	0.17	141.1	105.0	77
PP 3 (PP 3F)	205	12.7	1.16	112,000	86 (85)	1.8 (2.0)	0.27	0.08	0.18	135.0 (135.4)	97.4 (100.8)	67 (70)
PP 4 ^a	205	11.8	1.01	90,000	85	2.0	0.29	0.07	0.16	136.7	98.8	73
PP 5	205	24.8	2.06	70,000	85	2.0	0.27	0.08	0.16	125.2	85.7	58
PP 6 ^b (PP 6F)	410	12.6	0.56	223,000	160 (155)	1.9 (2.0)	0.33	0.04	0.11	142.8 (142.7)	103.6 (108.2)	76 (81)
PP 7 ^{a,b}	410	12.0	0.62	264,000	155	2.0	0.30	0.06	0.11	142.3	106.9	77
PP 8 ^c (PP 8F)	240	12.2	0.93	92,000	125 (123)	1.9 (1.9)	0.30	0.00	0.08	137.4 (138.1)	101.3 (103.6)	71 (75)

Polymerization time = 10–45 min; stirrer speed = 1000 rpm; Al/Zr = 2000; catalyst = 0.2 μ mol; P = 0.5 bar; T = 60 °C. Values in parenthesis are the polymer properties after post-treatment.

^a 1-Dodecene as comonomer.

^b P = 1.0 bar.

^c T = 50 °C.

Though the polymerization medium heptane was replaced with toluene for the current study, our results (Table 3, PP1) were in the line with those obtained previously. As previously, the polypropylene was highly isotactic (>99.8%) and the stereochemistry was found to be controlled by enantiomorphous-site control. In addition, the microstructure was also very similar and the total amount of regio defects (2,1 and 3,1 misinsertions) was around 0.3–0.4%. The dominating chain termination reaction was chain transfer to aluminium, resulting in a molar mass defined mainly by the propylene concentration in the reactor medium.

In contrast to the copolymerization of olefins with highly functional monomers, no extra shielding (e.g. aluminium alkyl) was needed for successful copolymerization reactions of propylene and 7-octenyldimethylphenylsilane.

The 7-SiPh comonomer incorporated well into the polypropylene chain and there was a clear correlation between the comonomer concentrations in the feed and in the polymer. The catalyst activities were, however, reduced compared to the homopolymerization of propylene (PP 1 vs. PP 2, 3, 5), but the activities were at the same level as in the comparable copolymerizations of propylene and 1-dodecene (PP 3 vs. PP 4 and PP 6 vs. PP 7). This suggests that the decreased polymerization activity was due to the lower reactivity of the long comonomers, not due to catalyst poisoning.

The comonomers had no marked influence on the regio or stereo defects of the polypropylene and the molar mass was influenced mainly by varying the propylene concentration in the reaction medium, not by additional comonomers (PP 3 vs. PP 8 vs. PP 6). These variations in the propylene concentration in the reactor slightly affected

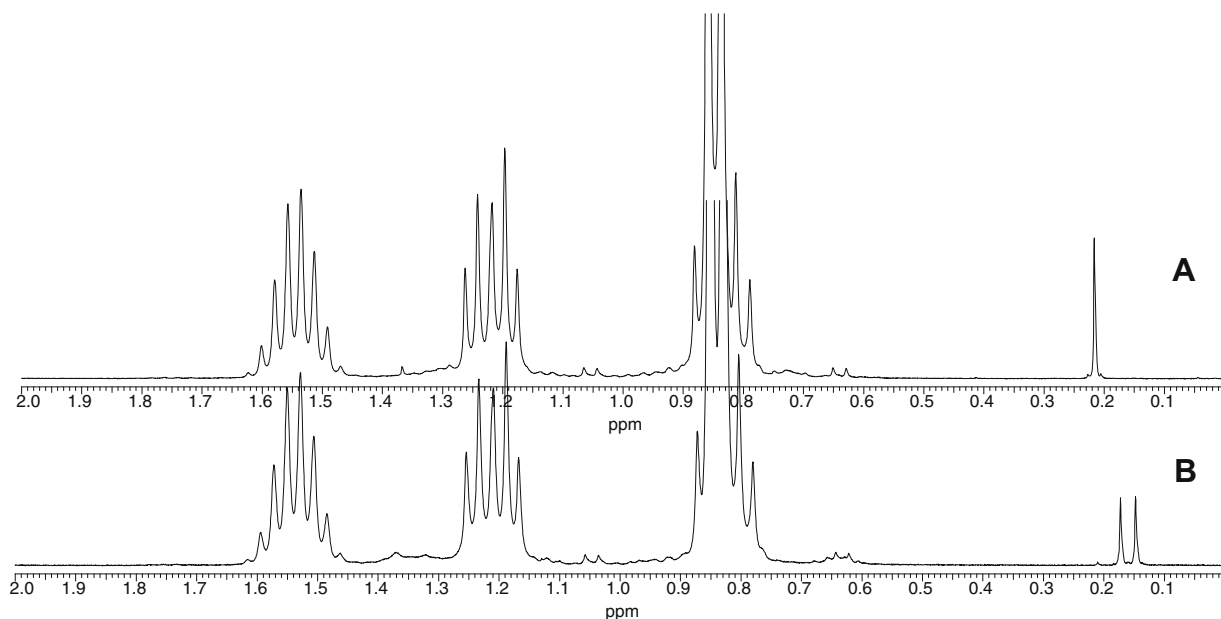


Fig. 3. ^1H NMR spectra of the polymer PP 3 before (A) and after (B) the protodesilylation step. The peak at 0.22 ppm (A) from the methyl groups of phenylsilane is replaced with a doublet ($J = 7.5$ Hz) at 0.17 ppm (B) from the methyl groups of fluorosilane.

the ratio of 2,1 vs. 3,1 misinsertions, as could be predicted. The 3,1 misinsertion is reported to form from isomerisation of the 2,1 misinsertion [29]. After the 2,1 misinsertion the active center is rather dormant and it then has time to isomerize into its more active/open 3,1-form. Reducing the time for isomerisation by increasing the propylene pressure in the polymerization reaction (or by decreasing polymerization temperature at a constant propylene pressure) would reduce the degree of 3,1 misinsertion.

3.1.3. Post-treatment

The post-treatments of copolymers were carried out without any antioxidants that could possibly interact with the post-treatment reagents. An antioxidant is usually required to prevent the decomposition of polypropylene when it is processed at elevated temperature. Decomposition was not a problem in our case and no indication of a yellow colour in the reaction medium, due to the decomposition of PP, was observed. Also, the measured molar masses (Table 3, values in parenthesis) remained at the level of the untreated copolymer. Thus it can be assumed that the post-treatment was not detrimental to the polymer.

The crystallization temperature of the copolymer was slightly increased (Table 3, values in parenthesis) after the post-treatment step. This phenomenon was probably due to some solid residues remaining in the copolymer, which acted as nucleating agents. This explanation is supported by a change observed in the profile of the melting curve (not presented here). The multiple endotherm, caused by melting–recrystallization–remelting in un-nucleated polypropylene [30], was clearly diminished, suggesting the presence of some kind of nucleator.

The success of the protodesilylation reaction was determined by ^1H (Fig. 3A vs. B) and ^{13}C NMR (Fig. 2A vs. B) and the conversions were found to be over 95%. The post-treatment of the copolymer changed the observed peak positions in the NMR spectra as expected. The peak assignment (Table 1, X = F) was done primarily by comparing the peak positions to those of a polyethylene analogue [25] and to the untreated PP-co-SiPh. The change of phenyl to fluoride influenced the ^{13}C NMR shifts over six bonds. The influence seemed to vanish for the C3 carbon (30.05 vs. 30.06), but a small (and real) difference was again observed between the C2 carbons (X = Ph vs. X = F, 27.00 vs. 26.96 ppm, respectively). In addition to changing the shifts, the fluoride split the peaks of the carbons (C6 and C7) attached to the silicon. That influence was also detected for C5 carbon (22.88 ppm), but the coupling was barely visible (Fig. 2B, inset 3).

3.2. The synthesised polypropylenes as modifiers in PP/ μSi composites

In our previous studies we have found that the synthesised silane groups (Si-Ph or Si-F) can interact either weakly or strongly with inorganic fillers in polyethylene-based composites [31]. In this study, we used comparable functional polypropylenes as modifiers in polypropylene/microsilica composites. They were expected to react or interact with the μSi filler and bind it more strongly to the matrix. Their reactivity could be observed through

their influence on the morphological, thermal and/or mechanical properties of the PP/ μSi composite. As a reference modifier we used a commercial grade functional polypropylene, PP-g-COOH.

3.2.1. Filler dispersion in the composites

The microscopy pictures of the selected samples are presented in the Fig. 4. The microsilica aggregates can be seen as dark areas in the picture taken from the master batch (Fig. 4A). The concentration of the microsilica in

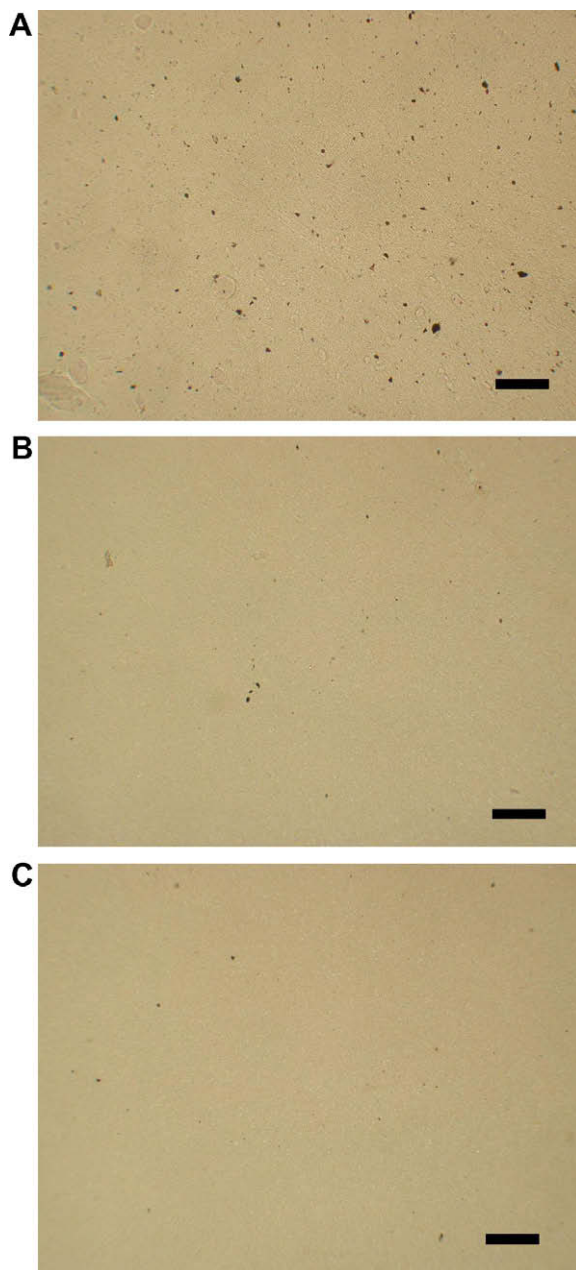


Fig. 4. Optical microscopy pictures of the selected samples: (A) PP/ μSi master batch (30 phr of μSi), (B) final PP/ μSi -composite (4 phr of μSi) and (C) PP/ μSi /PP-co-SiF (4 phr of μSi and 0.4 phr of PP 8 F modifier). The size of the black scale bar is 100 μm .

aggregated form was estimated to be only ~1% of the whole microsilica volume and the main part of the fillers were dispersed to the size not to be seen with the optical microscopy ($\lesssim 1 \mu\text{m}$). The aggregate formation was clearly decreased in the final composites (Fig. 4A vs. B), which was largely due to the lesser level of filler in the PP matrix. Still, there were some randomly distributed aggregates up to size of 5–20 μm and the aggregated silica concentration remained at the level of 1%. Otherwise than expected, the use of any of the modifiers did not make any visible change in the filler distribution (Fig. 4B vs. C).

3.2.2. Thermal properties of the composites

The crystallization temperatures of different composites are presented in Table 4. Microsilica alone did show some nucleation ability, as the crystallization temperature (T_c) of the PP-matrix was increased from 114 °C almost to 120 °C (C1 vs. C2, C3, C4) as the microsilica concentration went from 0 to 4 phr. The use of the commercial functional PP-g-COOH, PB1002, resulted in better adsorption of the matrix on the surface of the filler, as expected, and the crystallization temperature was increased a further ~7 °C (C2 vs. C5; C3 vs. C6; and C4 vs. C7). Surprisingly, the untreated PP-co-SiPh (PP6: C8, C9, C10) showed the same kind of behaviour, and to almost the same level, with the crystallization temperature reaching a maximum of ~126 °C (Fig. 5). When the phenylsilane group in the polypropylene was replaced with fluorosilane (PP 6 F: C11, C12, C13) the influence became even slightly stronger. Increasing the concentration of the functionality in the polypropylene (PP 6 vs. PP 8 and PP 6 F vs. PP 8 F) had no major influence on the crystallization temperatures, except that the difference between the untreated and post-treated forms (PP 8 vs. PP 8 F) became smaller.

3.2.3. Tensile properties of the composites

We also tested the mechanical properties of some of the composites. The variations in the tensile properties were small and usually inside standard deviations values (Table 4). The concentration of microsilica used was very limited and it was not influencing clearly properties other than the modulus. However, the small variations in yield strengths of composites were probably noteworthy, an interpretation that was further supported by the small standard deviations of these values. As the yield strengths of the unmodified composites (C2, C3, C4) and the composites modified with the commercial grade functional PP-g-COOH (PB1002: C5, C6, C7) were nicely at the level of 30 MPa, the addition of the untreated PP-co-SiPh (PP 8: C14, C15, C16) or the functional PP-co-SiF (PP 6 F: C11, C12, C13) increased the yield strength slightly. In general, the yield strengths of composites increase when e.g. a strong bond is formed between the matrix and fillers [2,4].

3.3. Coating of microsilica

To verify the interaction/reaction between the microsilica filler and the dimethylphenylsilane group in the side chain of polypropylene, we treated the silica fillers with molecular trimethylphenylsilane. As reference we used chlorotrimethylsilane which is known to react rapidly with hydroxyl groups at the silica surface, scheme 1A.

The reference reaction was run at 50 °C for 30 min. and the influence of chlorotrimethylsilane on the surface of microsilica was clearly seen in the DRIFT-spectra (Fig. 6A vs. E). Comparing the spectra of microsilica before and after the treatment show that the original O–H vibration at 3744 cm^{-1} from hydroxyl groups on the silica surface was replaced by C–H vibration originating from methyl

Table 4
Thermal and tensile properties of the PP/ μSi composites with and without adhesives (nm = not measured).

Comp.	Composition/phr			T_c (°C)	Yield		Modulus (MPa)
	HE125	μSi	Modifier		Strain %	Strength (MPa)	
C1	100	0	0	114.3	12.8 ± 0.3	29.1 ± 0.2	860 ± 30
C2	99	1	0	117.1	12.3 ± 0.3	30.0 ± 0.3	880 ± 30
C3	98	2	0	118.9	12.2 ± 0.2	30.0 ± 0.2	880 ± 20
C4	94	4	0	119.7	11.7 ± 0.3	29.9 ± 0.3	930 ± 30
			PB1002				
C5	99	1	0.1	124.7	12.3 ± 0.3	30.0 ± 0.2	900 ± 10
C6	98	2	0.2	126.2	12.2 ± 0.3	30.1 ± 0.1	910 ± 10
C7	96	4	0.4	127.2	11.7 ± 0.2	30.2 ± 0.1	930 ± 20
			PP 6				
C8	99	1	0.1	123.9	nm	nm	nm
C9	98	2	0.2	124.8	nm	nm	nm
C10	96	4	0.4	126.1	nm	nm	nm
			PP 6 F				
C11	99	1	0.1	125.6	12.5 ± 0.4	30.6 ± 0.1	900 ± 20
C12	98	2	0.2	126.9	12.3 ± 0.3	30.8 ± 0.2	910 ± 20
C13	96	4	0.4	127.9	12.0 ± 0.4	31.0 ± 0.2	950 ± 10
			PP 8				
C14	99	1	0.1	124.4	12.4 ± 0.2	30.5 ± 0.2	930 ± 10
C15	98	2	0.2	125.5	12.3 ± 0.3	30.5 ± 0.3	910 ± 20
C16	96	4	0.4	126.5	11.9 ± 0.3	30.4 ± 0.2	930 ± 20
			PP 8 F				
C17	99	1	0.1	125.1	nm	nm	nm
C18	98	2	0.2	125.7	nm	nm	nm
C19	96	4	0.4	126.5	nm	nm	nm

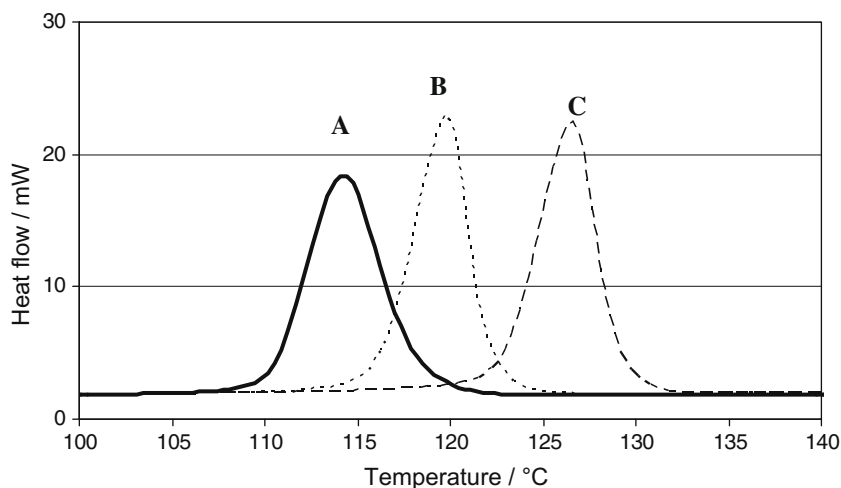
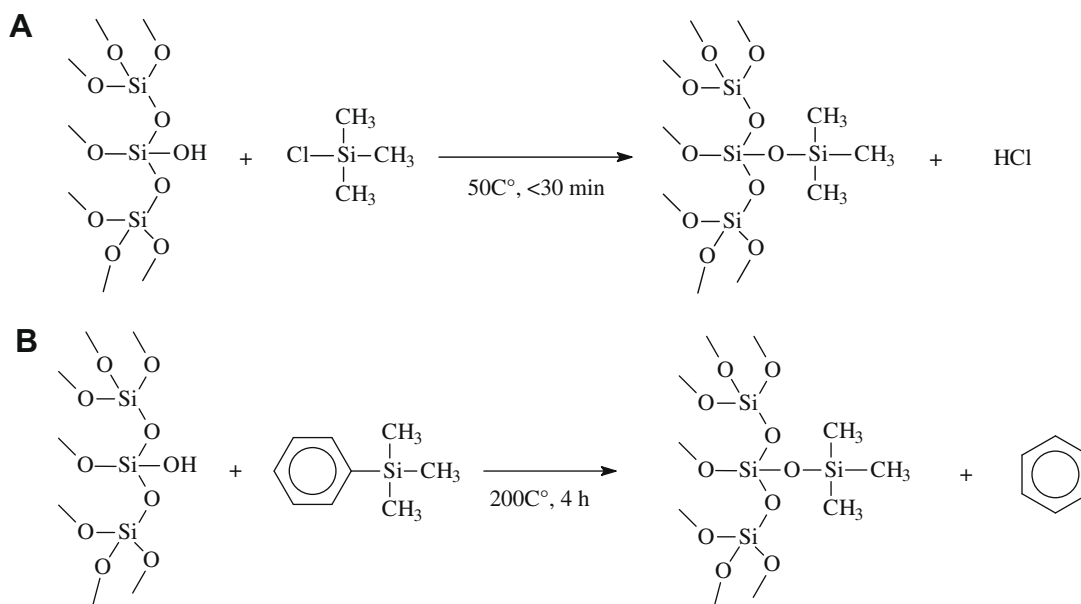


Fig. 5. The DSC-cooling curves of (A) PP, (B) PP/ μ Si-composite (4 phr of μ Si) and (C) PP/ μ Si/PP-co-SiPh composite (4 phr of μ Si and 0.4 phr of PP 6 modifier).



Scheme 1. The reaction between the free hydroxyl group at the silica surface and (A) chlorotrimethylsilane, or (B) phenyltrimethylsilane.

group (at 2964 and 2906 cm^{-1}). The (trimethyl)phenylsilane was found to react in a similar manner (scheme 1B), although more sluggish (4 h at 200 $^{\circ}\text{C}$; Fig. 6B, C and D), and resulting in same kind of surface chemistry on the microsilica filler. To promote this conclusion all specific vibrations originating from aromatic groups (3030, 1450–1600 cm^{-1}) or Ph-Si bond (1600, 1430 cm^{-1}) were absent. Finally this reaction was confirmed by finding the side product, benzene, from the reaction residue. The residue was analyzed with ^{13}C NMR and an additional peak was formed at 128.3 ppm which is characteristic for benzene.

4. Discussion

As observed previously [32], the silicon-containing comonomer, 7-SiPh, was found to copolymerize with

ethylene and at that time no influence of the phenylsilane comonomer on the metallocene catalyst was detected. In the present study, the more complex structure of the polypropylene allowed us to detect with greater sensitivity any possible influence of silicon. Nonetheless, no influence was found, as the formed microstructure of the polymer remained untouched when 7-SiPh was used as comonomer in polymerization with propylene. It still appears that the silicon itself has no influence, good or bad, on the metallocene/MAO catalyst system.

Some other studies have shown a clear decrease in molar mass when silanes were used in metallocene/MAO based polymerization [33–35]. However, in those studies, allylsilanes were used, and the observed influence derived from the β -effect of silicon (drives carbocation at the β -position of silicon). This effect makes β -hydride elimination

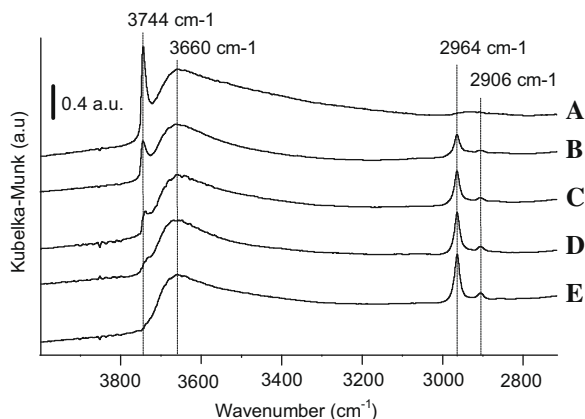


Fig. 6. DRIFT-spectra of the coated microsilia samples: (A) uncoated microsilia, (B) microsilia reacted with Ph-Si(CH₃)₃ for 60 min at 200 °C, (C) as B but 120 min at 200 °C, (D) as B but 240 min at 200 °C, (E) microsilia reacted with Cl-Si(CH₃)₃ for 30 min at 50 °C.

more favored after allylsilane insertion, resulting in depressed molar masses. The β -effect essentially only becomes important when the silicon is located near the double bond. It seems important to increase the spacer between silicon and the double bond to greater than one methylene group. In our monomer, the spacer is six methylenes, which is clearly sufficient. It still remains unclear what the minimum requirement is for spacer length to obtain acceptable polymerization of silicon-containing monomer with metallocenes.

The further use of functional polymers as modifiers in composites is based on their ability to react with the filler. The increased interaction between the filler and the matrix can often be observed in several varied properties of the composites. In this study, the influence of the different modifiers on the morphology of the composite was negligible, but the increased crystallization temperatures indicated significantly improved adsorption of the polypropylene matrix on the filler surface. Still, the variations in crystallization temperatures were not clearly influenced by the nature (Si-F vs. Si-Ph vs. COOH) of the reactive groups; even they were expected to react differently. As well known, the halo- and alcoxysilane groups can form a strong covalent bond with the hydroxyl group at the filler surface. The phenylsilanes react also in similar manner, although more sluggish as seen in this study. In contrast, the formation of weaker bonds (dipole-dipole, acid-base, hydrogen bonding) take place in the case of acids, esters or alcohols [36,37].

The influence of the modifiers on the mechanical properties was small and any major conclusion can not be drawn from them. The small increases in the yield strengths were not large enough to be explained solely by improved adhesion between the microsilia and the modifier. The reinforcing effect of filler alone may play some role as well. However, these small changes still support the above mentioned comprehension of different kind of reactivity between the microsilia and the modifier: the use of PP-co-SiF (PP 6F) or PP-co-SiPh (PP 8) increased slightly the yield strength of the composite in contrast to the negligible influence of PP-g-COOH (PB1002).

5. Conclusion

The metallocene catalyst, Me₂Si(2-Me-4-Ph-1-indenyl)₂ZrCl₂/MAO was found to be tolerant towards a silicon-containing comonomer, 7-octenyldimethylphenylsilane, in copolymerization with propylene. The response of the catalyst was found to be closely similar to the comparable copolymerization of propylene and 1-dodecene. Both of the comonomers incorporated well into the polypropylene chain but otherwise their influence on the microstructure formed was negligible.

The phenylsilane group in the side chain of polypropylene was easily changed to the extremely reactive fluorosilane group. The post-treatment was performed without causing any major changes in the properties of the copolymer (e.g. molar mass). In addition, both synthesised copolymers, PP-co-SiPh and PP-co-SiF, were found to be adhesion promoters in the composite of microsilia and polypropylene. The increases in crystallization temperatures of the matrices indicated a strong interaction between the filler and both copolymers. It also became obvious that (trialkyl)phenylsilane group is able to react with hydroxyl group of the microsilia filler. As a reactive group, phenylsilane may provide the possibility to polymerize reactive polyolefins with a metallocene catalyst directly without a post-treatment step, without a massive protection of the functional comonomer, and without a drastic decrease in catalyst activity and molar mass.

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