

Research Article

Functionalization of Silica Nanoparticles for Polypropylene Nanocomposite Applications

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Synthetic silica nanospheres of 20 and 100 nm diameter were produced via the sol-gel method to be used as filler in polypropylene (PP) composites. Modification of the silica surface was further performed by reaction with organic chlorosilanes in order to improve the particles interaction with the hydrophobic polyolefin matrix. These nanoparticles were characterized using transmission electronic microscopy (TEM), elemental analysis, thermogravimetric analysis (TGA), and solid-state nuclear magnetic resonance (NMR) spectroscopy. For unmodified silica, it was found that the 20 nm particles have a greater effect on both mechanical and barrier properties of the polymeric composite. In particular, at 30 wt%, Young's modulus increases by 70%, whereas water vapor permeability (WVP) increases by a factor of 6. Surface modification of the 100 nm particles doubles the value of the composite breaking strain compared to unmodified particles without affecting Young's modulus, while 20 nm modified particles presented a slight increase on both Young's modulus and breaking strain. Modified 100 nm particles showed a higher WVP compared to the unmodified particles, probably due to interparticle condensation during the modification step. Our results show that the addition of nanoparticles on the composite properties depends on both particle size and surface modifications.

1. Introduction

Polyolefin materials have grown to a crucial role in modern society, from daily life to high-performance engineering applications. The low cost of production, facile and inexpensive processability, and good properties of these materials have allowed them to replace some of the traditional more expensive and less adaptable materials. Moreover, the addition of organic and inorganic fillers has opened a wide field of research for new possible applications for these materials.

Over the last 20 years, there has been a strong interest in the study and development of polymer nanocomposites, where at least one dimension of the filler has nanometric dimensions. The high interest for these materials is the high effective surface of the nanosized filler making it possible to tailor and handle the properties of the material with very small proportions of the filler. Low loadings of silica nanoparticles (<10 wt%) in polymeric matrices can considerably improve the performance of these materials, such as mechanical, thermic, and barrier properties [1–3].

Traditionally, these nanocomposites have been widely studied by using natural aluminosilicate clays, mainly because of the high availability and low cost, with good results. Recent studies have shown that modified clays can reduce by 90% the permeability coefficient of different gases at 20 vol% of clay [2]. Nevertheless, synthetic particles have grown interest over the past decade, especially for food packaging and medicine applications, due to the absence of heavy metals and toxins in the particles. The sol-gel method is a good alternative for silica nanoparticle synthesis, being able to tailor the particles geometry and size [3–6]. The mechanism of the sol-gel method, using organic silanes as precursors, starts with hydrolysis of the functional groups, followed by condensation of the silanol groups. The mechanism is, of course, much more complicated and includes a number of parallel reactions such as the condensation of organic groups from the precursor. In basic conditions, hydroxyl groups acts as a catalysts. By controlling the pH of the reaction, it is possible to control particle size due to the relative rate at which both hydrolysis and condensation occur. At a high pH,

condensation occurs much more rapidly than hydrolysis, so fewer nuclei will be formed and the reaction will occur by monomer addition leading to larger particles [6].

Different studies have demonstrated the importance of the nanoparticles geometry and aspect ratio in the final properties of the nanocomposite material [1, 2]. However, aspect ratio is only one of the many different variables that must be taken into account in the study of these materials. Both size and effective surface of the nanofiller play a crucial role in the mechanical, thermal, and barrier properties of the material [3]. The level of filler dispersion within the polymer matrix and the level of adhesion and physical or chemical interactions between the filler and the polymer also plays an important role in the material final properties [7]. As discussed by Takahashi and Paul [8, 9], when untreated silica particles were incorporated in a poly(ether imide) matrix the permeability was increased due to the presence of voids in the particle-polymer interface, while surface-treated silica reduced the material permeability coefficient.

Different approaches have been developed in order to modify silica surface functionality, such as incorporation of compatibilizing agents such as maleic anhydride (PPgMA) [7], in situ polymerization of the polymer matrix in the presence of the inorganic filler [10], grafting of coupling agents in both silica and PP [11, 12], or by grafting reactions of the silanol groups on the surface of the silica particle with different compounds, such as organic silanes [13–15]. This produces a better interaction and dispersion of the silica particles in the polymeric matrix, and as a consequence an improvement in the composite properties [13, 14].

The main goal of this work is to synthesize silica nanospheres with different diameters and modify its surface by grafting reactions with chlorosilanes with various organic chain lengths, which will be used as filler in polyolefin matrices in order to study the materials mechanical and barrier properties.

2. Experimental

2.1. Materials. Tetraethoxysilane ($\geq 98\%$, TEOS), trimethylchlorosilane (97%, TMCS) and dimethyloctylchlorosilane (97%, DMOCS) were acquired from Sigma-Aldrich and used as received. Ammonia (25%) and heptane (99%, anhydrous) were acquired from Equilab. Polypropylene with a melt flow index (MFI) of 7.5 g/10 min (PP-H401) was obtained from Braskem and used as received. The antioxidant agent used in nanocomposite preparation was a mixture (2 : 1) of Irganox 1010 and Irganox 168.

2.2. Synthesis of Spherical Silica Nanoparticles via Sol-Gel Method. Silica nanospheres of different sizes were prepared using the sol-gel method, with TEOS as the precursor. The molar ratio of $\text{H}_2\text{O}/\text{TEOS}/\text{EtOH}$ was held constant at 4/1/8, while the amount of ammonia was changed for particle size control, using a molar ratio NH_3/TEOS from 0.03 to 0.35. A solution containing TEOS and 90% of the absolute ethanol was poured into a 2000 mL flat-bottom vessel equipped with a heating bath and a magnetic stirrer, while a second solution containing water, ammonia and the remaining ethanol was

added dropwise to it. The mixture was sealed and stirred for 5 h at $50 \pm 2^\circ\text{C}$ to obtain a silica sol. The solvent was then evaporated at 70°C , obtaining a fine white powder which was homogenized using an analytical mill at 10°C . Finally, the powder was calcined at 400°C for 8 hours.

2.3. Surface Modification of Silica Nanospheres. TMCS and DMOCS were used as grafting reactants, while heptane was used as reaction medium. Silica nanospheres were calcined at 400°C under vacuum for 5 h in a sealed round bottom flask in order to remove the adsorbed water on the silica surface and isomerize the silanol groups into the more reactive isolated silanol groups.

Heptane was poured into the flask and sonicated for 20 min in order to disperse the silica nanospheres in the heptane. After sonication, the corresponding chlorosilane was added into the flask, while maintaining a nitrogen atmosphere inside the flask. The TMCS modification occurred at 50°C for 24 h under constant stirring, while the DMOCS modification was performed under reflux for 24 h. The mixture was subsequently centrifuged to separate the powder from the solvent and rinsed with clean heptane in order to remove the unreacted chlorosilanes. The powder was finally dried at 150°C under vacuum for 5 h to remove the remaining solvent.

2.4. Characterization of the Modified and Unmodified Silica Nanospheres. The resulting silica nanospheres were characterized by TEM (JEOL 1011 operated at 100 kV) and BET surface analysis (Micromeritics ASAP 2010 Physisorption Analyzer, pretreatment at 200°C) in order to establish the particle diameter and specific surface. Elemental analysis (Leeman Labs Inc. CE440 elemental analyzer and Control Equipment Corporation 440), TGA (SDT (TGA-DSC) Q600, $20^\circ\text{C}/\text{min}$ under N_2), and ^{29}Si CP MAS NMR spectroscopy (Bruker AVANCE 300, 4 mm double resonance broadband probe using a MAS rate of 10 KHz) were carried in order to verify and quantify the effect of the surface modification.

2.5. Nanocomposite Blending. The PP/SiO₂ nanocomposites were produced by melt mixing in a Brabender Plasti-Corder at 190°C and 110 RPM for 10 min. Approximately 35 g per mixing was produced, containing PP, SiO₂ nanoparticles, and a small spoonful of Irganox 1010: Irganox 168 (2 : 1) as antioxidant. Mixture was then flattened in a cold hydraulic press to solidify and was then cut into smaller pieces of ca. 5 mm.

2.6. Mechanical Properties of Nanocomposites. Samples were prepared by melt pressing of the material at 190°C and 50 bar in a heated hydraulic press for 5 min. Samples were then cooled using a water cooling system, solidifying the sample and releasing the pressure. Test samples were cut from these sheets using a stainless steel die in a hydraulic press, obtaining a 12 cm \times 1 cm and 1 mm thickness testing samples, according to the ATSM D638. Mechanical properties were measured using an HP D500 dynamometer with a strain rate of 50 mm/min at room temperature. Young's modulus was

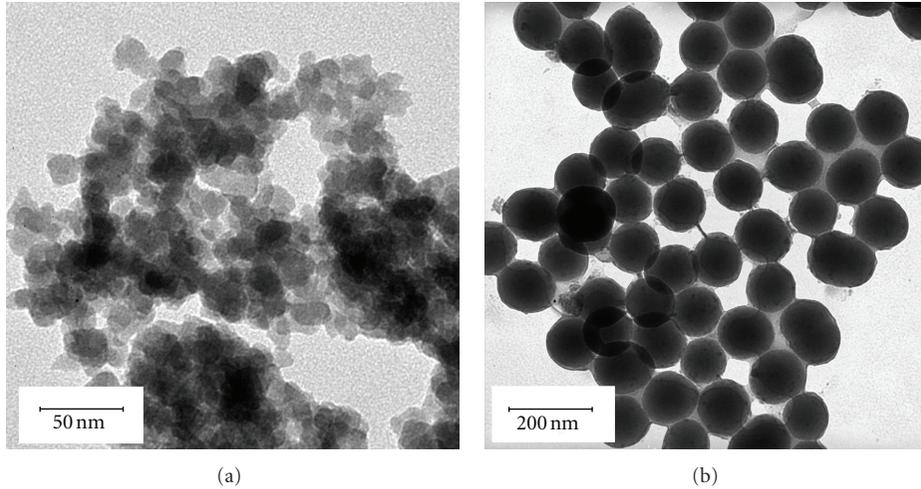


FIGURE 1: TEM images of SiO_2 nanospheres synthesized via sol-gel method. (a) NS20. (b) NS100.

TABLE 1: Silica nanospheres diameter and specific surface.

Sample	Molar ratio NH_3/TEOS	TEM diameter (nm)	BET surface (m^2/g)
NS20	0.03	22 ± 4.3	287 ± 0.7
NS100	0.35	113 ± 13.5	41.7 ± 0.2

calculated as the slope of the linear elastic zone on the stress-strain curve. Breaking strain is defined as the last point of the curve before the stress abruptly falls to a value of zero.

2.7. Water Vapor Permeability. Samples for barrier properties were prepared by melt pressing the material at 190°C and 50 bar in a heated hydraulic press for 5 min using a 0.2 mm stainless steel mold. The system was then cooled using a water cooling system to solidify the samples. Circular test samples of diameter 3.5 cm were cut off from the film.

The water vapor permeability (WVP) was measured using the dry cup method [16]. Aluminum sample cups, equipped with rubber o-rings, were filled with 2 g of phosphorous pentoxide and covered with a 3 cm diameter film of the polymer sample and top secured above. The total mass of the cups was measured and then placed in a sealed chamber with a 90% relative humidity and 20°C . The mass of the cups was measured every 24 h for a minimum of 15 days. The daily weight uptake of each cup corresponds to the water vapor that has permeated through the polymeric film, thus the slope of the graph “weight versus time” corresponds to the water vapor transmission rate. Water vapor permeability was calculated using the formula (1) expressed below:

$$\text{WVP} = \frac{e * 100}{A * P_{\text{sat}} * \text{RH}\% * \text{PM}_w} \left(\frac{dm}{dt} \right), \quad (1)$$

where e corresponds to the film thickness, A is the effective area of the polymer film, P_{sat} is the saturation pressure of water at the given temperature, $\text{RH}\%$ if the relative humidity at the sealed chamber, PM_w is the molecular water, and dm/dt is the slope of the weight/time curve after system has reached

the steady state condition (linear region). WVP is expressed in $\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$.

3. Results and Discussion

3.1. Sol-Gel Synthesis. Two sets of silica nanospheres were successfully synthesized via sol-gel method and characterized by various techniques. TEM images of the spherical silica particles synthesized are shown in Figure 1. By changing the molar ratio NH_3/TEOS and, therefore the pH of the reaction medium, the final size of the synthesized silica nanospheres was controlled (Table 1), resulting particles of approximately 20 and 100 nm, named as NS20 and NS100, respectively (NS stands for nanosilica, while number stands for particle average diameter). A higher pH in the reaction medium results in a higher yield due to the basic catalysis, and larger particles due to the ionization of the condensed species causing growth to occur by monomer addition rather than particle aggregation [6].

3.2. Silica Surface Modification. Modification of silica nanoparticles was performed in order to improve the particle-polymer interaction when used as fillers in polyolefin nanocomposites, such as polypropylene. These modified particles were characterized in order to establish the effective addition of carbon chains into the silica surface. Reaction occurs in the silica surface between the silanol groups and the alkylchlorosilane, grafting the alkylsilane to the surface of the silica via Si–O–Si bonding releasing HCl in gas form (Figure 2).

The solid state ^{29}Si CP MAS NMR spectra of the modified and unmodified silica particles are presented in

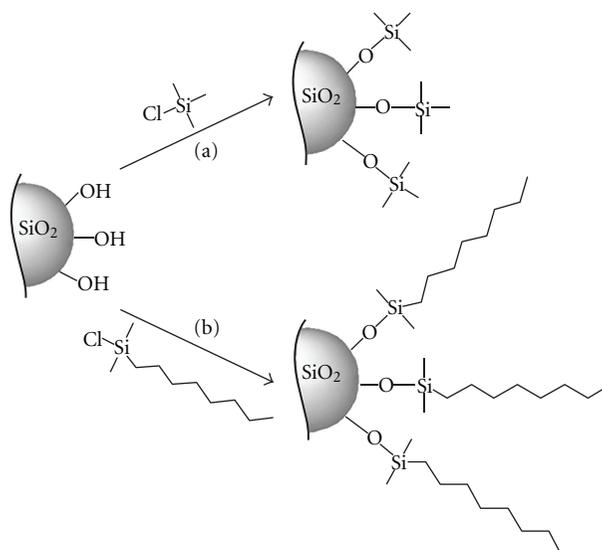


FIGURE 2: Modification of the silica surface via grafting reaction with (a) TMCS and (b) DMOCS.

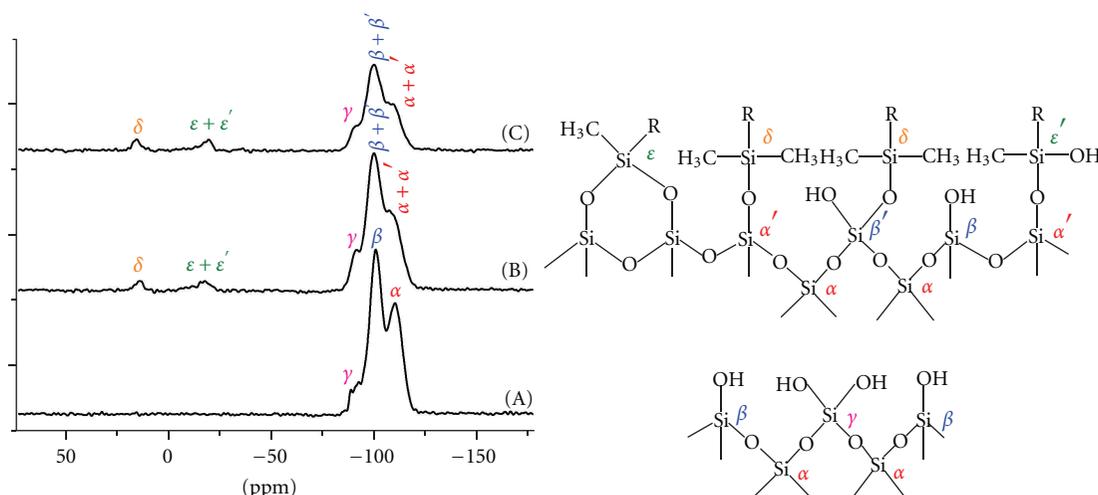


FIGURE 3: Solid state ^{29}Si CP MAS NMR spectra for the unmodified (A) and modified 20 nm particles with TMCS (B) and DMOCS (C). The notation “R” at δ , ϵ and ϵ' corresponds to methyl (TMCS) or octyl (DMOCS) groups.

Figure 3. Unmodified silica (Figure 3(A)) presents 3 characteristic peaks: -110 ppm (α), corresponding to silicon from $\text{Si}(\text{OSi})_4$, -100 (β), and -90 ppm (γ), corresponding to free and germinal silanol groups, respectively. After modification with both TMCS and DMOCS, the number of silanol groups was diminished, as the line intensities β and γ were decreased [13, 14]. Smaller peaks appear on both modifications at $+15$ (δ) and -16 ppm (ϵ and ϵ'). The first (δ) corresponds to the silicon from the chlorosilanes reactants, now grafted to the surface of the particle via Si–O–Si bonding, with 3 organic groups attached to it (three methyl for the TMCS and two methyl and one octyl group for the DMOCS) as presented in Figure 2. The second chemical shift at -16 ppm ($\epsilon + \epsilon'$) corresponds to silicon from the chlorosilanes reactants that have lost one of their organic groups, leaving a free OH group, or attaching itself to adjacent silicon via Si–O–Si

bonding. The loss of one of these groups may occur after a heating treatment at high temperatures, such as the drying of the particles at 150°C after the modification was performed [14]. These results confirm the success of the surface modification of the silica surface by grafting of the organic silanes. The absence of peaks near $+30$ ppm shows that all of the unreacted chlorosilane was successfully removed in the washing stage after modification.

Table 2 shows the results of elemental analysis of the unmodified and modified silica particles. The low carbon content on unmodified silica particles comes from unreacted TEOS and ethoxy groups that were not fully oxidized by calcination of the particles (400°C). The carbon content of modified silica is higher because of the grafting of chlorosilanes on the surface of the particles containing organic groups. For the DMOCS modified silica, the carbon

TABLE 2: Carbon content from elemental analysis of silica nanospheres.

Particle size	Modification	Carbon content (%)
20 nm	—	0.91%
	TMCS	3.04%
	DMOCS	4.74%
100 nm	—	0.44%
	TMCS	0.63%
	DMOCS	2.92%

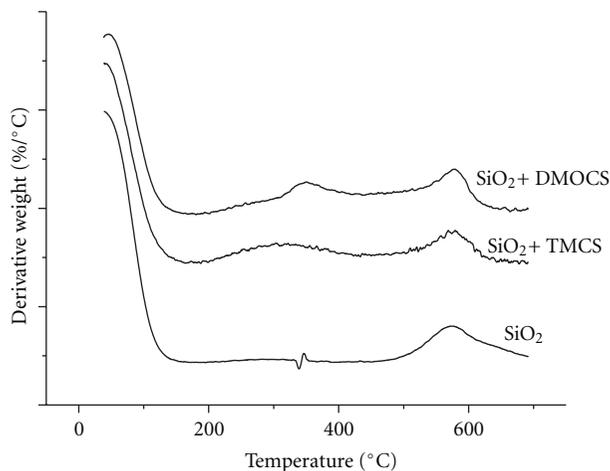


FIGURE 4: Derivative of thermogravimetric analysis (TGA) of NS100 samples. Tests run 20°C/min under N₂. From bottom to top: unmodified, TMCS modified, and DMOCS modified silica.

content is higher because of the large carbon chain of the octyl group.

The incorporation of organic groups in the silica is further confirmed by TGA of NS100 samples in Figure 4. Results showed that unmodified silica particles lose up to 4.3% of their total mass at 200°C, which corresponds mainly to adsorbed water at the hygroscopic surface, while the TMCS and DMOCS modified silica only lose up to 2.9 and 2.7% of their mass at the same temperature. Because of the presence of organic hydrophobic groups in the modified silica surface, water cannot be as easily adsorbed as it is on the unmodified silica. In the 200 to 450°C, unmodified silica particles show a small linear loss, corresponding mainly to vicinal hydroxyls condensation on the silica surface [17–19], while modified silica also start losing the organic groups grafted to the surface, showing a peak in the differential weight loss curve [18, 19]. This analysis confirms that DMOCS has a higher carbon content than TMCS modified silica. Finally, above 450°C silica loses the rest of the silanol groups, especially free silanol groups. The NS20 samples showed similar results.

3.3. Nanocomposite Blending and Mechanical Properties. Unmodified silica of 20 and 100 nm were used to prepare 10, 20, and 30 wt% nanocomposites with polypropylene, whereas TMCS and DMOCS modified silica of 100 nm and

TMCS modified silica of 20 nm was used to prepare 10 wt% nanocomposites.

Results from mechanical testing are shown in Figure 5. For both 20 and 100 nm particles, Young's modulus is increased (Figure 5(a)) and breaking strain is highly decreased with the addition of unmodified silica (Figure 5(c)). The increase in the Young's modulus and decrease in the breaking strain are more significant for the 20 nm particles due to the higher specific surface of these, with an increase in Young's modulus up to 70% at 30 wt%.

For 100 nm particles, surface modification of the silica did not affect Young's modulus considerably (Figure 5(b)); nevertheless, with both TMCS and DMOCS modification, the breaking strain increased to almost twice the value of the unmodified silica nanocomposite (Figure 5(d)). This effect is caused due to the presence of organic groups in the silica surface acting as coupling agents in the particle-polymer interface giving greater mobility to polymer molecules around the SiO₂ nanoparticles in the composite under tensile stress conditions. The TMCS modified 20 nm silica composites presented a lower increment in breaking strain than larger particles, but also resulted in an increment in Young's modulus. This increase in Young's modulus could be caused by a better adhesion level between of the modified silica surface and the PP matrix. Similar results were obtained by Panaitescu et al. [20] for PP/SiO₂ nanocomposites using styrene-(ethylene-co-butylene)-styrene triblock copolymer as compatibilizer between the silica nanoparticles and the PP matrix.

3.4. Water Vapor Permeability. For the water vapor permeability test, it was found that unmodified silica increases the WVP, mainly due to the hygroscopic nature of the silica surface, which increases the solubility factor of the vapor in the polymer, thus increasing the permeability (Figure 6(a)) [3]. This effect is greater for the smaller 20 nm particles due to the larger specific surface, increasing the WVP up to a factor of 6 at 30 wt% compared to the neat PP matrix.

Modification of the silica surface with alkylsilanes should decrease the silica affinity toward water by making the silica surface more hydrophobic, therefore decreasing the solubility factor and the permeability. Modified 100 nm silica composites were studied (Figure 6(b)), presenting greater permeability coefficients compared to the unmodified particles, increasing WVP to twice its value compared to unmodified silica composite. This effect may be caused due to interparticle condensation during the modification step, forming agglomerates and increasing the polymer free volume and creating void channels, thus increasing the permeability for water vapor [8, 9].

4. Conclusions

Silica nanospheres of 20 and 100 nm diameter were synthesized via the sol-gel method, using TEOS as the precursor. By changing the reaction medium pH, it was possible to control the final size of the nanoparticles. Modification of the silica surface was successfully performed by grafting reactions with organic chlorosilanes. Solid-state ²⁹Si CP MAS

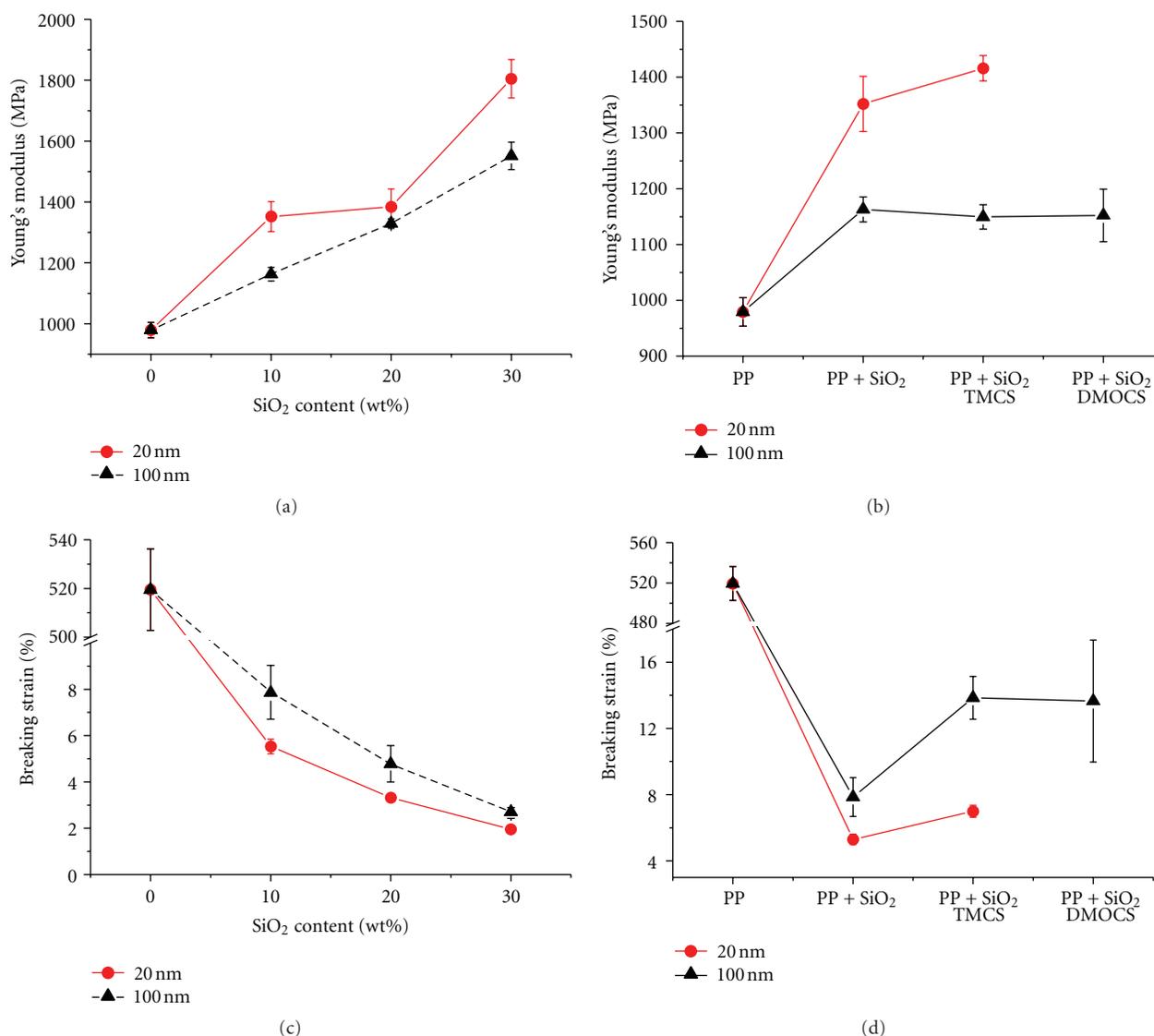


FIGURE 5: Mechanical properties of modified and unmodified SiO₂/PP nanocomposites. (a, c) Young's modulus and breaking strain of unmodified SiO₂ nanocomposites; (b, d) Young's modulus and breaking strain of modified SiO₂ nanocomposites (10 wt%).

NMR spectroscopy, elemental analysis, and TGA confirmed the effective modification of the silica surface with both TMCS and DMOCS.

PP nanocomposites were prepared using unmodified and modified silica particles. The addition of these particles increases the Young's modulus of the original PP matrix, but it highly decreases the breaking strain of the material. The smaller 20 nm particles had a greater effect both on the increase of the Young's modulus and on the decrease of the breaking strain, mainly due to the higher specific surface. Surface modification for the 100 nm particles did not affect Young's modulus, but considerably increased the breaking strain of the composite due to the presence of organic groups in the silica surface. TMCS modified 20 nm particles showing a small increase in the composite breaking strain and Young's modulus due to a better adhesion level between the modified particle's surface and the polymer matrix. In

barrier properties, it was found that the addition of silica increases the WVP of the material, due to the hygroscopic nature of the silica surface. However, modification of the 100 nm silica particles did not reduce the WVP but increased it probably due to interparticle condensation during the modification step increasing the polymer free volume.

These results show that the addition of nanoparticles on the final properties of the polymeric composite depends on both particle size and surface modifications.

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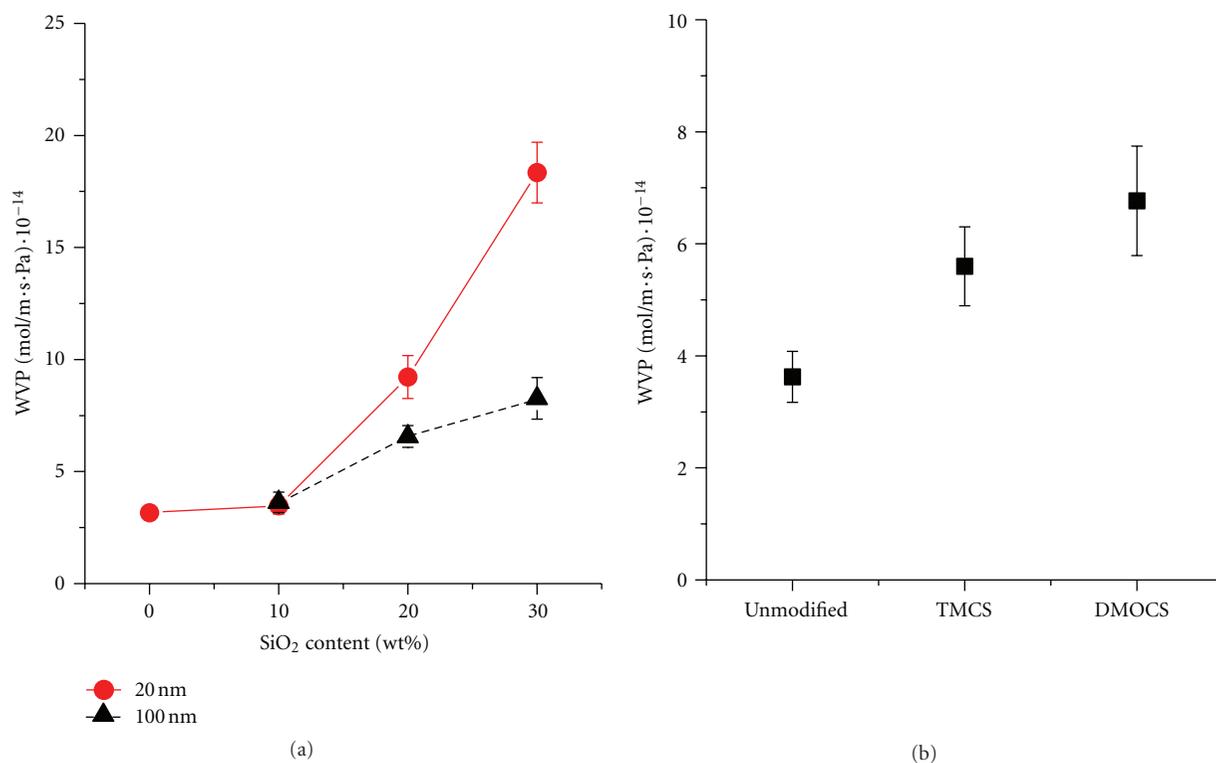


FIGURE 6: Water vapor permeability of the prepared nanocomposites: (a) unmodified silica of 20 and 100 nm; (b) modified and unmodified silica of 100 nm at 10 wt%.

Elemental Analysis (Facultad de Química, Pontificia Universidad Católica de Chile, Chile); Dr. Jason M. Spruell (MRL, University of California Santa Barbara, USA) for solid-state CP MAS ²⁹Si NMR analysis.

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