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FUNCTIONALIZATION OF SILICA NANOPARTICLES FOR POLYPROPYLENE NANOCOMPOSITES APPLICATIONS

Diego Bracho^{*1}, Vivianne Dougnac², Humberto Palza¹, Raúl Quijada¹

1 – Departamento de Ingeniería Química y Biotecnología, FCFM- Universidad de Chile- Santiago, Chile

2 – Departamento de Química, Facultad de Ciencias- Universidad de Chile- Santiago, Chile

Abstract - Synthetic silica nanospheres of different diameters produced via the sol-gel method were used in order to enhance the barrier properties of the polypropylene-silica nanocomposites. Modification of the silica surface by reaction with organic chlorosilanes was performed in order to improve the particles interaction with the polypropylene matrix and its dispersion. Unmodified and modified silica nanoparticles were characterized using electronic microscopy (TEM), elemental analysis, thermo gravimetric analysis (TGA), and solid state nuclear magnetic resonance (NMR) spectroscopy. Preliminary permeability tests of the polymer-silica nanocomposite films showed no significant change at low particles load (3 wt%) regardless its size or surface functionality, mainly because of the low aspect ratio of the silica nanospheres. However, it is expected that at a higher concentration of silica particles differences will be observed.

Keywords: *Nanocomposites, silica-nanoparticles, sol-gel, grafting, permeability.*

Introduction

Polymer-silica nanocomposites are opening new aspects of applications for plastic materials. Low loadings of silica nanoparticles (~2 wt%) in polymer matrices can considerably improve the performance of these materials, such as its barrier properties [1,2]. The use of nanoparticles alters the total free volume where gas particles are absorbed in the polymer matrix changing the solubility coefficient, and creating a tortuous path by interfering with the gases free path of diffusion [2].

Traditionally, the study of these materials for gas barrier applications has been approached by using natural aluminosilicate clays, mainly because of the high availability and low cost, with good results, reducing the permeability coefficient by 90% of the original at 20 vol% [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 [3,4]. Surface functionality can be tailored by grafting reactions of the silanol groups in the surface of the silica particle with different compounds, such as organic chlorosilanes, in order to get a better interaction and dispersion of the silica particles in the polymeric matrix and the inorganic particles, and by consequence the effect over the composite barrier properties.

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 polypropylene (PP) matrices to evaluate the barrier properties of the composites.

Experimental

Synthesis of spherical silica nanoparticles via sol-gel method

Silica nanospheres of different sizes were prepared using the sol-gel method, with tetraethylorthosilicate (TEOS) as the precursor. Molar ratio H₂O/TEOS/EtOH was held constant at 4/1/8, while the amount of ammonia was changed for particle size control, using a molar ratio NH₃/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 drop wise to it. The mixture was sealed and stirred for 5 h at 50±2°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.

Surface modification of the silica nanospheres

Trimethylchlorosilane (TMCS) and dimethyloctylchlorosilane (DMOCS) were used to be grafting reactants. Heptane was mixed with 6 g of the silica particles in a 500 mL round-bottom flask. The mixture was then heated to 50-55°C in a temperature controlled heating bath provided with a magnetic stirrer in a nitrogen environment. TMCS (or DMOCS) was added drop wise into the mixture and allowed to react for 24 h. For the modification with TMCS the reaction occurred at 50°C, while the DMOCS modification was performed using reflux. Subsequently the mixture was centrifuged and washed several times. The powder was then dried under vacuum for 5 hrs at 150°C.

Particle characterization and verification of surface modification

TEM images were taken in order to measure the nanospheres diameter, while solid state ²⁹Si CP MAS NMR (Cross Polarized Magic Angle Spinning Nuclear Magnetic Resonance) measurements, thermo gravimetric analysis (TGA), diffusive reflectance infrared fourier transform (DRIFT) spectroscopy and elemental analysis were performed in order to establish the effect of the grafting reactions.

Nanocomposite preparation

Silica particles were dried under vacuum for 5 h at 150°C prior to use. Polypropylene-silica nanocomposites were prepared by the melt-mixing process in Brabender mixer at 190°C and 110 RPM for 10 minutes, using a small spoonful (ca. 30 mg) of Irganox 1010: Irganfox 168 (2:1) as antioxidant.

Permeability measurement

Nanocomposite films samples for permeability measurements were prepared by melt pressing the samples at 190°C to a thickness of ca. 0.2 mm. Permeability was tested using a permeation cell built in our laboratory, described in detail elsewhere [5]. The cell is a hermetic closed system, consisting of two chambers separated by the film sample. The first chamber is under vacuum, while the second one contains the gas to be tested at approx. 2 bar. Changes of the total pressure in both chambers are measured by two different manometers over time. Permeability coefficient is calculated using the time-lag technique Eq. 1 [6].

$$P = \left(\frac{V_b \cdot e}{A \cdot T \cdot p_a} \right) \frac{dp_b}{dt} \quad (1)$$

Where P is the permeability coefficient, V_b is the volume of the low pressure chamber, e is the film thickness, A the film surface, T is temperature, p_a is the pressure of the incoming gas, and dp_b/dt is the slope of the pressure/time curve of the low pressure chamber.

Results and Discussion

Two sets of silica nanospheres were successfully synthesized and characterized. TEM images (Fig. 1) show the spherical silica particles synthesized, 22 nm diameter, with a standard deviation of 19%, and 113 nm diameter, with a deviation of 12%.

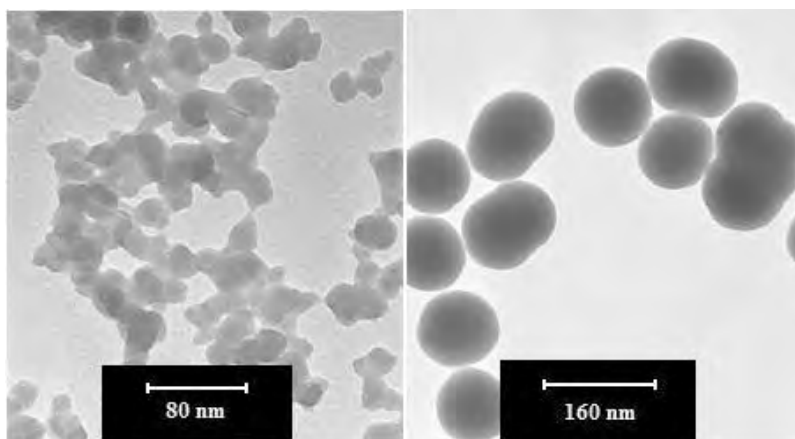


Figure 1 – TEM images of SiO₂ nanospheres synthesized via sol-gel method. On the left: 22 nm diameter spheres. On the right: 113 nm diameter spheres.

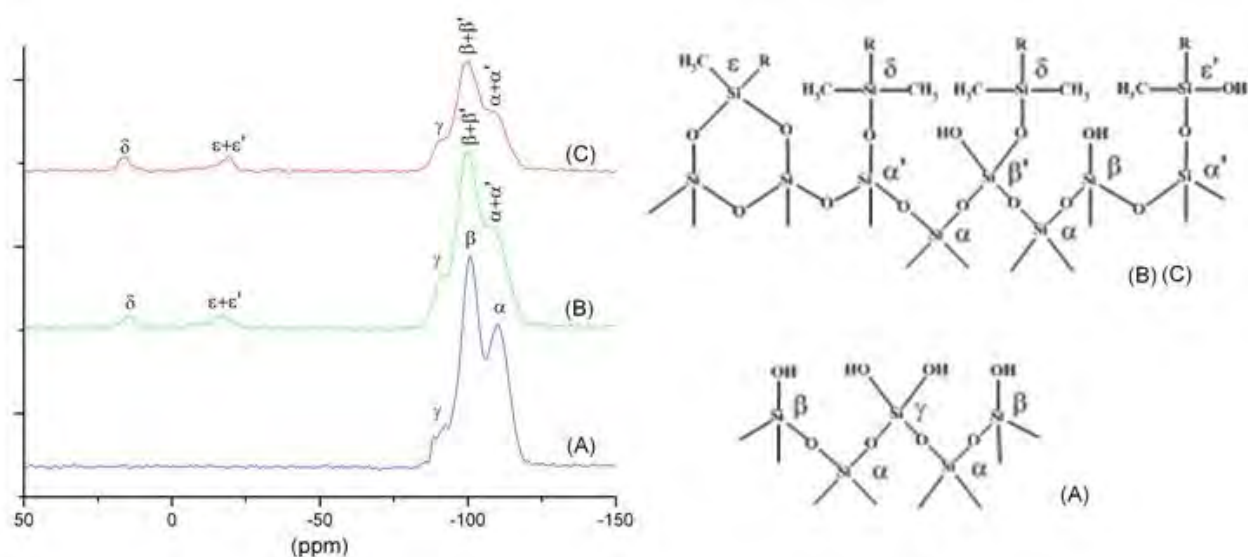


Figure 2 – Solid state ^{29}Si CP MAS NMR spectra for the unmodified (A) and modified 22 nm particles with TMCS (B) and DMOCS (C). The notation ‘R’ at δ , ϵ and ϵ' corresponds to methyl (TMCS) or octyl (DMOCS) groups.

The solid state ^{29}Si CP MAS NMR spectra presented on Fig 2 show that after the modification, with both TMCS and DMOCS, the number of silanol groups has diminished, as the line intensity decreases at -100 (β) and -90 ppm (γ), corresponding to free and germinal silanol groups respectively [7]. Resonance at -110 ppm corresponds to $\text{Si}(\text{OSi})_4$ (α). 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 an octyl group for the DMOCS). 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 [7]. These results confirm the success of the surface modification of the silica surface by grafting of the organic silanes.

Table 1 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 silicas is higher because of the grafting of chlorosilanes on the surface of the particles containing organic groups. For the DMOCS modified silicas the carbon content is higher because of the large carbon chain of the octyl group.

Table 1 – Carbon and hydrogen content from elemental analysis of silica nanospheres

Particle size	Modification	Carbon content (%)
22 nm	-	0.91%
	TMCS	3.04%
	DMOCS	4.74%
113 nm	-	0.44%
	TMCS	0.63%
	DMOCS	2.92%

The results from TGA analysis showed that modified silica particles in the range of 200 to 700°C lose up to 4% of their total mass when being modified with DMOCS and 2.3% with TMCS. These values correspond mainly to the organic groups of the grafted silanes when the surface functionalization is done. The mass loss is greater for the DMOCS modified particles due to the presence of a long chain octyl group in opposition to the methyl group in TMCS. Infrared spectroscopy (DRIFT) for the modified silica particles showed the appearance of peaks in the 3000 cm^{-1} range, which corresponds to the carbon-hydrogen absorption band. For the DMOCS modification these band shows more intense peaks due to the presence of the octyl group. TGA and DRIFT spectroscopy will be presented in the congress, which are jointly in agreement with the solid state NMR spectroscopy results presented on Fig. 2.

Preliminary oxygen permeability measurements show no significant changes in the permeation coefficient of oxygen by adding 3 wt% of silica nanospheres, regardless the particles diameter or the surface functionality (Fig. 3). Because of the low aspect ratio of the nanospheres ($\alpha=1$), tortuous path mechanism has a low impact on the gas diffusion through the film. The high increase of the permeability coefficient of the polypropylene- DMOCS modified silica was mainly because of high particles agglomeration due to moistening creating a free path for the oxygen to permeate. However, it is expected that a higher concentration of silica particles will result in a larger change in the permeability coefficient, so that the effect of the silica surface modification and particle size will be observed.

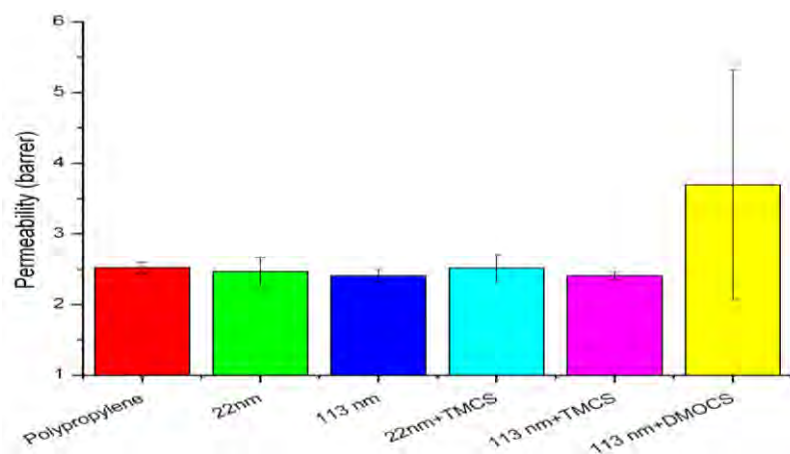


Figure 3 – O₂ permeability measurement of polypropylene-silica nanocomposite films (3 wt%).

Conclusion

Silica nanospheres of different sizes were synthesized via the sol-gel method by changing the reaction medium pH. Modification of the silica surface was successfully performed by grafting reactions with organic chlorosilanes. The use of silica particles for nanocomposite films at low charges (3 wt%) has no significant impact on the films permeability coefficient, regardless the particle size or surface functionality. Further work will include the use of higher concentrations of silica particles.

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