Controlled formation of spheres by phase segregation in hybrid organic-inorganic PMMA–SiO₂ systems through the silane coupling agent GLYMOS

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The use of coupling agents in a PMMA–SiO₂ system, synthesized from TEOS and using diethyl oxalate (DO) as a solvent for PMMA, generates uniform and transparent coatings with good adhesion. The use of DO as a solvent for both phases made the system compatible, and a transparent composite was formed. The introduction of a silane coupling agent usually increases compatibility among organic and inorganic phases and also adhesion to the substrate. Nevertheless, in the case under study, a silane coupling agent (γ-glycidoxypropyl trimethoxysilane, GLYMOS) was used because of the observed effect of increasing the size of emulsion droplets, usually on a nanometric scale. The main characteristic of the composite system consisted of a high density of perfectly formed PMMA spheres wrapped in a silica matrix. These were regularly uniform in both distribution and particle size. Frequently, there were one or two main sizes. High control in sphere size was attained through the GLYMOS content. TGA and contact angle measurements were carried out, comparing coatings made of SiO₂, PMMA, hybrid using DO, and hybrid using DO with GLYMOS.

Keywords: ORMOCERs, hybrid, sol-gel, SiO₂, silane coupling agents.

1. Introduction

Nowadays, there is increasing use of nano-and micro-structured materials. There is a growing interest in developing and using hybrid materials, seeking to satisfy increasing needs and applications that have great versatility and potential by combining properties inherent to organic polymers or inorganic components. Extensive work has been performed in this area, where silane coupling agents (SCA) frequently appear, mainly as adhesion promoters [1]. Optical transparency, scratch resistance, corrosion protection and other multi-functional characteristics are commonly desirable properties.

In the sol-gel study area, establishing scheme for naming structures based on their number of oxygen bonds to each metal atom is being established. A metal with 4, 3, 2, and 1 oxygen substitutions (with corresponding organic replacement) is called a "Q", "T", "D" or "M" resin, respectively. In the case of silicon, a Q pure resin is SiO₂ or quartz, a silsesquioxane resin is a T, a siloxane resin is a linear D, and M is a siloxy group. The ceramic community conceptualizes organic-inorganic hybrids as organically modified silicas, referring to them as ORMOSILs (organically modified silanes), Ceramers, ORMOCERs(organically modified ceramics), Polyceramers, Nanomers, etc. [2-4]. To some extent, these materials combine the most important properties of their constituents, such as high transparency (glass-like), low processing temperatures(plastics-like), sufficient thermal stability (silica-like) and easy accessibility since their base materials are widely available.

Comparing a purely inorganic gel with one that has been organically modified, the latter can improve the original mechanical properties, water resistance and film forming capacity with the benefit of not compromising optical transparency. Moreover, the organic-inorganic hybrid can improve a purely organic gel by improving its mechanical properties (hardness, abrasion resistance) and gas and liquid impermeability. In addition, depending on the precursors, the hybrid is capable of obtaining high adhesion between constituents and the substrate. Several polymers, such as poly(methyl methacrylate, PMMA), poly (styrene), poly (vinyl acetate), poly (vinyl pyrrolidone), poly (dimethyl siloxane), epoxies and polyimides have been reported as having excellent optical clarity when incorporated into an inorganic network by the sol-gel process. In general, coupling agents are used to introduce chemical bonds between organic and inorganic phases [5].

Many types of organic coatings lose up to 85% of their initial adhesion under watery conditions [6,7]. In addition, adhesives show a marked loss of bond strength in water [8], and glass fiber reinforced composites degrade rapidly as well. In order to improve initial bond strength between adhesives or coatings and substrates, adhesion promoters(coupling agents) can be used to improve substrate wettability or to create secondary links by Vander Waals forces, dipole-dipole interactions, hydrogen bonding or acid-base reactions, involving relatively weak forces in the range of 5-8 kcal/mol. The use of a coupling agent capable of forming chemical bonds at 50-250 kcal/mol is required to achieve a bond hydrolytic stability [9].

Co-hydrolysis with tetraethoxysilane incorporated Q units into silsesquioxanes is recognized. Introduction of a monomer with epoxy substitution (glycidoxypropyl trimethoxysilane, GLYMOS) allows better outer wetting and
adhesion to polycarbonate lenses and incorporation of silica sols. Many ORMOSILs have been proposed as scratch-resistant coatings [10] and anti-reflective layers for eyeglasses [11].

In conventional composite systems, coupling agents may function as surface finishing modifiers, sealants or adhesives, depending on the thickness of the cross-linked material at the interface. A coupling agent is expected primarily to improve adhesion between organic and inorganic components and to increase property retention under a variety of circumstances. A coupling agent is a compound capable of reacting chemically with both the polymer and the substrate.

In many works, coupling agents have been used to reduce phase separation between organic and inorganic components. In this study, we achieved organic-inorganic phase coexistence at a nanometer level without the use of coupling agents. Instead, a coupling agent was mainly used to achieve control of phase segregation size and corresponding sphere formation effects as they grow from nanometric to micrometric sizes. Transparent solid coatings were obtained with adherence to metallic and glass surfaces. Four kinds of coatings were produced: SiO₂, PMMA, PMMA-DO/SiO₂, and PMMA-DO/SiO₂/SCA. The latter was the only coating with micrometric sphere formation. DO acted as the solvent in common for both PMMA and SiO₂ organic and inorganic polymers.

Sphere formation was controlled by the SCA concentration. Other SCAs may show similar effects but with varying concentrations. This may prove useful for templates, such as inverse opals applied to maximize areas of composite materials with active properties useful in various applications. The study focused mainly on a 1:1 ratio for organic and inorganic content. The resulting composite materials were transparent.

2. Experimental

The hybrid solution was prepared using tetraethyl orthosilicate (TEOS,C₈H₂₀O₄Si), 98%, Aldrich as a source of silica (SiO₂), poly(methyl methacrylate) of mₘ ~ 350,000 (CH₂=C(CH₃)COOCH₃), and a silane coupling agent of 3-glycidoxypropyl trimethoxysilane (GLYMOS), 98% Aldrich. The following solvents were used: ethanol (CH₃CH₂OH) (EtOH) J.T. Baker, diethyl oxalate (C₆H₁₀O₄ or C₂H₅OCOCOOC₂H₅), 99% Aldrich, and deionized water. HNO₃ was used as a catalyst to accelerate the poly-condensation reaction. The substrates used were glass slides or stainless steel.

The precursor solution for the sol-gel silica was composed of tetraethyl orthosilicate (TEOS) 98%, water and ethanol, prepared with a molar ratio of 1:4:3.33, respectively. The composition is conducive to good adhesion of coatings to metallic substrates because of its low water content. In addition, this low water content is appropriate for making the hybrid with a hydrophobic constituent, while still obtaining consistent coatings with adhesion to silica and metallic substrates. The TEOS was dissolved in ethanol using magnetic stirring for 20 min. Water was then added while maintaining constant stirring for 5 min. Finally, the acid was added as a catalyst, stirring for 10 min at room temperature (25 °C).

PMMA was dissolved in diethyl oxalate, at a ratio 1:4 v/v. The capped container with the polymer-solvent mixture was kept in a water bath for about 3 h at 65 °C with constant magnetic stirring. The result was a transparent polymeric solution with a viscosity around 42,000 cp.

The (PMMA-SiO₂) hybrid solution was prepared by mixing both sol-gel silica and dissolved PMMA. The mixture was prepared by adding sol-gel solution dropwise into the polymer with stirring until obtaining a clear solution. The methodology was different for solutions of HIB-SCA. PMMA was mixed with GLYMOS and then with the sol-gel silica solution, maintaining constant stirring for 10 min. The solution was aged for 12 h and subsequently deposited on silica or metal substrates by the dipping method.

The molar ratios for hybrid solutions with SCA and PMMA:SiO₂:GLYMOS were 1:1:0.05, 1:1:0.1 and 1:1:0.25. The former yielded better adhesion to metal substrates. All prepared coatings were obtained by the dipping method on steel substrates, using with a constant withdrawal speed of 3.2 mm/s. They were subsequently heat treated at 110 °C for 30 min. The final coatings obtained had good adhesion and high transparency and were free of fractures.

3. Results and Discussion

3.1 Hybrid material coatings analyzed by SEM

The coatings were characterized by scanning electron microscopy (SEM) in order to study the morphology of the coatings obtained. Fig. 1 show micrographs corresponding to the coatings: a) SiO₂ and b) PMMA/SiO₂ hybrid made using DO but without SCA. There was not a clear difference between the two.
Fig. 1 SEM micrographs corresponding to: a) sol-gel, b) hybrid SiO₂/PMMA without SCA. The images were taken at 1000 X, and scale bars represent 10 μm.

Figs. 2a and 2b show micrographs of hybrid-GLYMOS formulations containing SCA and DO, where results show an effect caused by the presence of GLYMOS/DO manifested as a formation of spherical particles. It is well known that the effect of surfactants is a reduction of the interfacial tension between phases due to adsorption at the liquid-liquid interface assembling a bulk solution into micelles. This reduces size and augments the population as the surfactant concentration rises. On the other hand, in this study, SCA increase caused a drop in the number of spheres and increased their size. This can be explained by considering that, using a concentration of 25% of the total solution and maintaining a constant fifty-fifty ratio of PMMA-SiO₂, SCA was preferably conforming spheres. The spheres were surrounded by a thin layer of the matrix, which indeed was composed mainly of SiO₂ with a small content of SCA, with increased adhesion to the substrate.

Fig. 2 Hybrid-GLYMOS SEM micrographs taken at: a) 1000 X and b) 5000 X. The scale bars represent 20 μm and 5 μm, respectively.

The hybrid-GLYMOS was deposited as transparent films by dip coating on stainless steel and glass. The GLYMOS/SiO₂/PMMA system generates optically transparent coatings at a macroscopic level. The materials include silica synthesized from tetraethyl orthosilicate (TEOS) and diethyl oxalate (DO) as a solvent for PMMA. Fig. 3a shows an image where spheres were presumably predominantly formed by PMMA, with SCA located at the interface with the matrix, presumably formed predominantly by SiO₂. The hybrid components and preparation procedure formed a system composed of a high density of perfectly formed spheres and uniform particle size, although there were generally one or two predominant sizes (as evident in Fig 3a). The spheres were surrounded and joined together through the silica matrix. This can be peculiarly seen in this image, where superficial cracks caused by the SEM electron beam during analysis start to form. A characteristic of this system was that self-forming spherical particles were positioned in a
disordered fashion without maximizing the occupied volume. Areas with higher matrix content were present, which in Fig. 3a appear as dark spaces.

The coupling agent had an evident effect on particle formation, particularly in size, morphology and distribution. Microanalysis shows the presence of the main elements (C, O and Si) corresponding to formulation components (Fig. 3b, from right to left with descending intensity: Si, O, and C, respectively. Fig. 3b also shows the GLYMOS structural formula at the upper right corner).

The SEM images are constructed by an electron beam that strikes a surface and through which surface topography can be displayed. It is important to note that observed spheres were approximately 1.5μm in size (scale bar corresponds to 1μm), with others of approximately 0.5μm in size, evident in images under a layer that was semitransparent to electrons. In addition, fractures caused by electron beams were observed. The position of the external surface was evidenced, and almost all forms appearing in the SEM images are bulk structures. The dark areas of the image are deep sections of a predominantly inorganic polymeric silica matrix. This is unusual in allowing observation of spheres produced within bulk material.

The observation of spheres as clear areas in a two-dimensional image (which in SEM corresponds to sites with high electron reflection) below surfaces of possibly PMMA/SCA occurred due to dispersion in their surface area and non-transmission of electron beams through the spheres’ own bulk. It can be also associated with a difference in density of both regions (spheres and surrounding matrix), together with percolation of electron beams within the coating, which reflects electrons and allows their detection and image reconstruction.
Fig. 4 Effect of GLYMOS content on PMMA–SiO₂ hybrids: a) 0.2%, b) 2%, c) 5%, d) 8%, e) 20%, and f) 25% v/v. All micrographs were taken at 2000 X, and the scale bars represents 10 μm.

Fig. 4 shows SEM images obtained for hybrid-GLYMOS, keeping constant a fifty-fifty ratio of PMMA and SiO₂ as a function of SCA concentration. Proportions were related to a total volume of a) 0.2 %, b) 2%, c) 5%, d) 8%, e) 20%, and f) 25%. It could be seen that sphere size increased as the GLYMOS concentration was raised. There were almost no cases of significant changes in shape or particle size heterogeneity. Even in the case of high coupling agent content, there was not direct contact between spheres, since each sphere was covered by the matrix.

It should be stated again that the nominal composition of SiO₂ and PMMA remained unchanged for these tests. In all images, but particularly evident in those corresponding to 20% and 25% GLYMOS (Fig. 4e,f), spheres occupied volumes exceeding those of any single component. This could even exclude a possibility of spheres formed only by SCA-SiO₂ and of these being joined together by the PMMA component.

The SEM characterization made it clear that the use of a coupling agent promotes an increase in the size of the micelles, always present in this type of hybrid, from a nanometric to a micrometric scale, although in no case were typical observed sizes greater than 3μm. The lead roles in hybrid sphere/matrix conformation were played by the solvent DO, in conjunction with a SCA. The images corresponding to pure PMMA and PMMA–GLYMOS do not show a similar phenomenon. In the case of a PMMA–SCA, such as GLYMOS, we begin to appreciate the different configurations of a single surface of SiO₂–GLYMOS. This leads to consideration of the fact that the coupling agent, in conjunction with the DO, participates in changing the surface tension in the interface of the nanometric micelles, allowing their junction and growth (Fig. 4).

The mixed solution of a hydrophobic organic and a hydrophilic inorganic component usually causes segregation of the organic phase. The silane coupling agents have been used to make these two components compatible, forming a Class I hybrid with an emulsion formed by nanometric micelles. This can be dried, maintaining a transparent coating or a monolith.

Unconventionally, the organic solvent used for the PMMA serves as a mutual solvent for both organic and inorganic phases. This is evident in the Class I hybrid SiO₂–PMMA without a coupling agent, of which coatings achieve adherence to surfaces of different natures, such as glass, acrylic, stainless steel, copper, brass, and aluminum. The considerably large difference in surface energies and roughness between these types of substrates prevents attaining coatings with good adhesion in most sol-gel materials.

It is noteworthy that the PMMA proportion was similar to SiO₂ in these hybrid materials, which can easily tilt towards one side or the other in composition for a final solid phase. Even more remarkable is that the regularly used 5% coupling agent was sufficient to show the effects of sphere formation.
It is remarkable that, even when spheres were observed by SEM, the coatings were optically transparent. In some cases, a slight whitish alteration appeared. Considering sphere sizes in the range of 100 to 2,000 nm for systems with DO/SCA, light scatters in most cases in nature, giving a white appearance to the materials or emulsions (milk, clouds, opals, Al₂O₃ and SiO₂ in suspension, etc.). This could be attributed to a narrowing of the difference among the refractive indices of PMMA (n₉PMMA=1.46) and SiO₂ (n₉SiO₂=1.37) systems when composed with SCA/DO.

There was not a hexagonal close packing order for spheres, which usually results when they are piled in a vessel. For example, polymerizing monomer micelles in an aqueous emulsion forms spherical particles that can be precipitated for an opal-like conformation, which can be used as a template for photonic crystals. Both the opals and photonic crystals have a hexagonal close packing order. The difference lies in that the hybrid originates as an emulsion, which passes to a solid form without further significant change. This places the spheres formed in an order that did not maximize the volume occupied. Nonetheless, at a similar level as in an emulsion, there was a particular uniformity in the distribution of spheres and a narrow particle size distribution. Also, the distance between particles had a very small standard deviation.

These hybrid materials were composed mainly of PMMA and SiO₂, forming spheres and matrix, respectively. The SCA together with DO was participating in conforming these spheres. Immersion in organic solvents did not alter the hybrid, which was certainly modified by hydrofluoric acid. This makes these hybrids potential templates for inverse opals, which can be used as a template for photonic crystals. Both the opals and photonic crystals have a hexagonal close packing order. The difference lies in that the hybrid originates as an emulsion, which passes to a solid form without further significant change. This places the spheres formed in an order that did not maximize the volume occupied. Nonetheless, at a similar level as in an emulsion, there was a particular uniformity in the distribution of spheres and a narrow particle size distribution. Also, the distance between particles had a very small standard deviation.

3.2 Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to analyze hybrid formulations of PMMA–SiO₂–SCA in solution in order to observe temperature dependent changes associated with a curing process and to determine whether the PMMA Tg was modified.

The stability brought to PMMA–SiO₂ solutions with other silane coupling agents extends beyond a period of one year in closed containers with no observed changes. Their gelation was mainly dependent on the catalyst content used for its sol-gel component. In contrast, the solutions with the silane coupling agent GLYMOS in closed containers precipitated as spheres, with sizes of tens to hundreds of microns in periods of one to several months using similar amounts and types of sol-gel catalyst. This implies that spheres continue to grow slowly until they achieve a size that makes them precipitate. Their appearance was like transparent beads. Transparent supernatant solutions contained colloidal spheres, as well. Fig. 5 shows the particle size distribution for spheres in this supernatant solution. Two peaks were present, one centered around 47 nm (range: 19 – 98 nm) and the other centered at 190 nm (range: 98 – 380 nm):

![Particle size analysis corresponding to an aged GLYMOS solution.](image)

TGA and DTA were applied to identify the solids content of the precipitated beads and supernatant, respectively. Fig. 6a shows differential thermal analysis of a supernatant corresponding to an aged solution (1 year) of 10% hybrid–GLYMOS. For this measurement, we used 10.63 mg of solution at a heating rate of 10 °C/min. The total weight loss in the range presented in the graph, 25 °C to 500 °C, was 9.19 mg, which represents 86.45%. This implies a solid residue of 13.55% in the supernatant. As already indicated, this can potentially be used for shaping inverse opal structures to make photonic crystals by metal electrodeposition or to make materials with uniform, controllable and non-crystalline macro- and meso-porosity. These porous materials may represent an advantage that helps these structures to be viable for extensive use as coatings.
Fig. 6 a) DTA, b) TGA, and c) DSC analysis of a hybrid-GLYMOS in solution.

Fig. 6b shows a TGA corresponding to hybrid-GLYMOS with some mass changes at different temperatures. Changes within the first 100 °C are attributed to solvent loss. Meanwhile, a slight change in slope in Fig. 6c corresponds to the glass transition temperature (Tg) for PMMA. The Tg determined experimentally for PMMA content in our hybrid material was around 122 °C, which shows similar results to the Tg corresponding to a m\textsubscript{w} of ~350,000 (120 °C).

The results obtained by TGA and DSC show that the components of the hybrid in solution retain characteristics possessed by each component, while in the coatings after drying, there was a greater resistance to decomposition under thermal annealing. This can be explained by a silica matrix embedding PMMA particles, which confers on them increased resistance to relatively high temperatures.

3.3 Contact angle analysis

The contact angle of a liquid on a surface is always a result of equilibrium of forces, mainly the liquid-substrate adhesion force vs. the cohesive strength of molecules composing the liquid. Likewise, the contact angle has both physical and chemical components. In the first case, it results from surface roughness, total area and distribution of contact points, on which a drop is supported. In the second case, the chemical affinity of the upper monolayer of a solid directly interacts with the liquid molecules. Contact angle measurements were conducted with water at room temperature (approximately 25 °C).

As a guide to identify the dominant character of the surface as hydrophobic or hydrophilic, we can consider imaginary lines at 0º, 45º, 90º, 135º and 180º. We start with a completely wet surface at 0º and finish with a spherical drop supported on a point on the surface substrate at 180º.

Table 1 shows information for contact angle tests for different coatings obtained by immersion in solutions, from left to right SiO\textsubscript{2} by sol-gel, PMMA dissolved in DO, hybrid SiO\textsubscript{2}-PMMA, and hybrid with a SCA GLYMOS. In each sample, there were four measurements; consequently only their averages are shown in Table 1. Finally, we emphasize that coatings were deposited on flat glass slides (Rw ~0.002 \(\mu\text{m}\)). Their surfaces of low roughness ensure that observed contact angle measurements were mainly the effect of chemical interactions.

According to data presented in Table 1, the contact angle of the silica coating was low (\(\theta_c \approx 36.2^\circ\)), as expected due to a hydrophilic surface. This kind of surface usually has good wettability. In contrast, the contact angle of a PMMA coating (m\textsubscript{w}=350,000) was in a hydrophobic regime, with an approximate value of \(\theta_c = 78.6^\circ\). It should be noted that this value can be highly dependent on the molecular weight of polymeric chains composing the surface, since with higher molecular weight, a PMMA becomes more hydrophobic and possesses higher static charge on surface. In the case of SiO\textsubscript{2}-PMMA hybrid coatings, we could expect an intermediate value according silica or polymer content. Nevertheless, it had a contact angle of an average of five degrees higher (\(\theta_c \approx 83.3\)) than PMMA, which turned out to be surprising. Table 1 presents in detail results of tests conducted for hybrid SiO\textsubscript{2}-PMMA coatings. This may indicate the presence of SCA in the outer surface. It can be seen that the coatings with GLYMOS maintained approximately similar contact angles than those of hybrids without SCA. Other SCA may show higher, similar, or lower contact angles.

The effect caused by coupling agents in a hybrid depends on its functional groups and on their concentration on the surface. The industrial use of coupling agents is with the intended purpose of increasing adhesion at the substrate-coating interface and, at the same time, increasing cohesion in the structure of the latter. Also, we should keep in mind that within a coating, the component distribution could be heterogeneous and that the drying process leaves a denser surface. Therefore, the same amount of SCA at outer, middle or bottom coating sites cannot be directly assumed.
Table 1 Contact angle measurements on the coatings of SiO$_2$-PMMA hybrid, and hybrid-GLYMOS.

<table>
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<tr>
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<th>SiO$_2$</th>
<th>PMMA</th>
<th>Hybrid</th>
<th>Hybrid-GLYMOS</th>
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<tr>
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<td>0.14</td>
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<td>Factor of Average Sphericity</td>
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<td>1.374</td>
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<tr>
<td>Average Volume [mm$^3$]</td>
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<tr>
<td>Contact Angle (left/right) [°]</td>
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<td>36.12</td>
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<td>Average Contact Angle (left/right) [°]</td>
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4. Conclusions

Silane coupling agent influenced hybrid material structure, promoting a formation of transparent spheres on the micron scale, visible only by SEM. They were mainly composed of PMMA and distributed in a matrix mainly composed of SiO$_2$, with such combination defining coating properties. The SCA was located at interfaces, including the outer coating surface.

The hybrid solution of PMMA-SiO$_2$ with a 1:1 molar ratio showed the best characteristics of homogeneity, high transparency, absence of fractures and chemical stability, as well as good adhesion to glass and other substrates. The use of diethyl oxalate (DO) as a solvent allowed compatibility among aqueous sol-gel silica and hydrophobic PMMA. The hybrid solution of PMMA-SiO$_2$ with a 1:1 molar ratio showed characteristics of homogeny, high transparency, absence of fractures and chemical stability.

In this study, we highlight four facts: 1) formation of spheres in the (PMMA/OD)-(SCA)-(SiO$_2$/EtOH/H$_2$O) system, 2) control in sphere size through the concentration of silane coupling agent or its type of functional group, 3) compatibility of hydrophilic and hydrophobic phases achieved through diethyl oxalate, and 4) observation of spheres in the bulk well below the surface in SEM images.

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