SYNTHESIS AND CHARACTERIZATION OF NEW HYBRID COPOLYMERS FOR HIGH PERFORMANCE COATINGS APPLICATION

A. Carvalho\textsuperscript{1}, E. Veludo\textsuperscript{2}, J. Machado\textsuperscript{2}, J. F. J. Coelho\textsuperscript{1} and M. H. Gil\textsuperscript{1}

Abstract
Polymeric hybrid materials and their specific functionalization have attracted great interest, due to their chemical, thermal and mechanical properties performance, in relation to their equivalent non-hybrids. Siloxane based materials offer great interest due to their excellent chemical, physical and electric properties. The primary structure of the siloxane could be modified either by side chain functionalization or by changing the main chain, forming hybrid materials. This kind of materials could be used in several and diverse areas, namely in protective and high performance coatings. The enhancement of their properties can be achieved by incorporating materials such as polyhedral oligomeric silsequioxanes (POSS) into their polymeric chain. In this paper are presented two new hybrid polymers, the poly(methyl methacrylate-co-isobutyl acrylate-co-glycidyl methacrylate-co-vinyltriethoxysilane) (POSS\textsubscript{0}) and the poly(methyl methacrylate-co-isobutyl acrylate-co-glycidyl methacrylate-co-vinyltriethoxysilane-co-isobutylo propyl methacrylate (polisilsesquioxane) (POSS\textsubscript{15}). These copolymers were prepared by a radical polymerization, and were designed to have the same structure acrylic, epoxy, silane and POSS fractions, which lead to offer multiple properties with high interest to coating systems due to their epoxy and siloxane groups.

The presence of the POSS cage in the hybrid polymeric structure increases the hydrophobic character and the thermal stability. When applied in commercial bi-component anti-corrosive paint formulations, the hybrid copolymers presented good performance, good compatibility properties for the different formulation components without forming agglomerates or phase separation. The coating formulation shows quick drying. These materials presented excellent mechanical properties, good adhesion, flexibility and impact resistance.

Keywords: Hybrid Materials, Radical Polymerization, POSS, High Performance Coatings

1. INTRODUCTION
Polymeric hybrid materials have attracted great interest due to their chemical, thermal and mechanical properties, when compared to their equivalent non hybrids polymers. These materials combine the advantageous properties of the organic materials, such as toughness, elasticity, durability and processability, with the interesting properties of the inorganic materials, such as hardness, chemical resistance and weatherability [1-4].

Silane based hybrids or composite materials offer suitable properties for protective coatings applications due to their excellent chemical, physical and electric properties. However, the weak interactions between silane and organic molecules avoid the formation of fibers and films. In order to overcome this problem, the primary structure of the siloxane can be modified either by side chain functionalization or by changing the main chain, forming covalent hybrid materials [5].

The preparation of these hybrid materials requires controlling the homogeneity of the two components [1]. This mixture between organic and inorganic phases could be obtained by incorporating acrylic polymers or oligomers into the inorganic matrix, by a simple physical mixture of the different parts (forming composites [6]) or by chemical polymerization of the acrylic and silane monomers (forming hybrid co-polymers [3, 5]).

Metallic corrosion phenomena occur via chemical reaction between the metal surface and the different species in the environment. Species as chloride or sulfate ions, oxygen and water, combined with the electron transport in the metal play an important action in the corrosion process [7-10]. In order to prevent the corrosion damage, different coating systems can be used. Depending on the most convenient option to each case, barrier coatings, inhibitive coatings and zinc-rich coatings can be applied [9, 11, 12].

Among several polymers used for anti-corrosive coatings, epoxy are suitable polymers due to their good mechanical and adhesion...
properties, excellent surface adhesion to metals (and other substrates) and good water, chemical and acid resistances [5, 13]. The epoxy, oxirane ring provides a site for crosslinking with proton donor species, such as amines, carboxyl and hydroxyl groups [13].

However epoxy resins present also some limitations since they are very sensitive to UV degradation, tend to lose gloss, present low thermal stability and low pigment binding stability and are hydrophobic. The copolymerization of epoxy resins with acrylic polymers, that brings other properties such as UV resistance, is an important route to mitigate the described problems [5, 13].

From a commercial standpoint epoxy materials are attractive since they are more effective against corrosion in thinner films than most other finishing materials. They are often used as primers in association with other materials which have good barrier properties but marginal adhesive characteristics. Epoxy polymers can be used in different types of formulations: one-component products that require high curing temperatures or using two-component being possible to promote the curing at ambient temperature [14].

In polymeric hybrid coatings, the epoxy properties could be combined with those of acrylic and silanes. Therefore, it is possible to combine in the same material the typical crosslinking density of epoxies, the heat resistance and superior weathering and water resistance of the silane, as the wide range of flexibility and the good UV stability from the acrylcs [13, 15]. The use of fillers as polyhedral oligomeric silsesquioxanes (POSS) can also improve the temperature and oxidation resistance, the surface hardening, decrease the flammability and the mechanical resistance of the hybrid materials [16].

In this study an epoxy-acrylic-silane hybrid copolymer was synthesized (Fig. 1). Each block segment of the hybrid copolymer is expected to play a specific role in the properties of the copolymer: the hardness of the material will be given by the methyl methacrylate (MMA), the flexibility by the isobutyl acrylic (BA), the reactive sites by the glycidyl methacrylate (MAG), and the adhesion properties by the vinyltrihexoxysilane (VTES). The purpose of the methacrylate isobutyl POSS (iBu-POSS) monomer addition is to increase thermal stability of the final polymeric material and due to its compatibility with the other co-monomers in the system.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate (MMA), isobutyl acrylate (BA) and glycidyl methacrylate (MAG) were purchased from Sigma Aldrich.

To the storage of the monomers it is added an stabilizer/inhibitor, namely hydroquinone, which must be removed before use. The inhibitor was removed from the MMA and BA monomers by a liquid/liquid extraction with an aqueous solution of sodium hydroxide (NaOH) and sodium chloride (NaCl), and from the MAG by passing through a column containing as stationary phase sand/alumina/sand. Vinyltrihexoxysilane (VTES) was purchased from Sigma Aldrich and methacrylate isobutyl POSS (iBu-POSS) was purchased from Hybrid Plastics Company and used as received.

Benzoyl peroxide (BPO) was purchased from ACROS Company and used as received. A mixture of p-xylene isomers and dodecanethiol were ordered from Sigma Aldrich and used as received.

The hardener, an amino functional methyl phenyl silicone resin solution, was purchased from Wacker and used as received.

2.2. Synthesis methodology

The hybrid copolymers were prepared by solution polymerization, using as radical initiator BPO. The synthesis procedure was adapted from the work of [17], as following: a p-xylene solution (60 mL) containing 700 mg of BPO and 1 mL of dodecanethiol (as chain transfer agent) were introduced in a 250 mL four-necked flask. The system was purged during 30 min with N₂. Then, 10 mL of the previously purified monomers mixture (Table 1) was added to the reaction vessel. The mixture was heated up to 75 °C. Once the reaction temperature was reached 5 mL of the monomers mixture was added dropwise to the mixture during 2 h under N₂ atmosphere. The reaction was kept over reflux for more 3 hours, resulting in a viscoelastic solution.

Fig. 1- Chemical structures proposed for the hybrid copolymers prepared.
The particle size of the grind obtained was evaluated by a Hegmann Gauge, to get the desired fineness value around 25 μm (NP EN ISO 15244 [19]).

The viscosity of the copolymer paint at (23±1) °C was evaluated with a Brookfield Viscometer, using a R5 spindle at 20 rpm, according to ASTM D2196 [20].

### 2.4. Formulation of hybrid co-polymers based paints

The hybrid copolymers prepared in this work were used to prepare a two component anticorrosive paint. The first component is the paint containing the hybrid copolymer in a standard formulation (Table 2). The hybrid copolymer, dispersants, fillers, solvent and pigments were placed in a ball mill machine and homogenized with a high speed Cowles disperser for 20 minutes. The first component was mixed with the hardener in the proportion of 3:1. The final viscosity of the mixture was evaluated.

### 3. RESULTS AND DISCUSSION

#### 3.1. Hybrid copolymers chemical characterization by ATR-FTIR

The extension of the polymerization reaction was evaluated by FTIR. The absorbance of the functional groups from the monomers and from the hybrid copolymers was measured in the range 4000-500 cm⁻¹. The FTIR spectra obtained for the two hybrids materials, POSS_0 and POSS_15, are presented in Fig. 2. From the analysis of the Fig. 2 it is possible to verify the absence of the band corresponding to the double bond, at ~1625 cm⁻¹, which suggest no residual monomer in the mixture. It is also possible to observe the displacement to lower wavenumbers, of the band maximum from 1148 cm⁻¹ to 1108 cm⁻¹ corresponding to POSS_0 and POSS_15 respectively. This displacement could be dependent on the influence from the vibrations due to the POSS cage in the copolymer structure. It is also possible to observe the presence of the glycidyl oxirane ring symmetrical and asymmetrical vibration bands in the shoulder present at 1250 cm⁻¹ and in the bands present at 950-810 cm⁻¹ respectively [21-24].

![Infrared spectra obtained for the hybrid copolymers prepared (POSS_0 and POSS_15) and theoretical vibration bands for this kind of chemical groups.](image-url)
3.2. Chemical characterization by $^1$H-NMR

From the spectrum obtained for the POSS_0 (Fig. 3) it is possible to observe the presence of the epoxy group protons ($\delta = 3.19$ ppm, $\delta = 2.26 - 2.46$ ppm) and the silane protons at ($\delta = 0.95$ ppm, $\delta = 1.07$ ppm and $\delta = 3.90$ ppm). Following the results obtained by FTIR no peaks related vinyl monomer groups at $\delta = 4.5 - 5$ ppm has been detected.

From the spectrum obtained for the POSS_15 (Fig. 3) it is possible to ascribe at $\delta = 3.19$ ppm and $\delta = 2.75$ ppm the signals from the protons of the epoxy group and the signals from the ethoxy group, linked to the silane, at ($\delta = 3.78$ ppm; $\delta = 1.10$ ppm and $\delta = 0.95$ ppm).

Since the hybrid copolymers prepared only differ in the presence or absence of the iBu-POSS co-monomer, it is possible to compare the obtained spectra. By overlapping the POSS_0 and POSS_15 spectra (Fig. 3), some differences were found, namely, the increase of the signal at $\delta = 2.26$ ppm (from the $-(CH_2)_2-$ protons of the iBu-POSS monomer) and the new signal at $\delta = 0.65$ ppm corresponding to the $-CH_2-$ protons linked directly to the POSS cage [25-27].

The Fig. 4 shows the assignment of the different NMR peaks for the POSS_15 copolymer.

3.3. Surface energy determination by contact angle measurement

The films used for the determination of the surface energy were prepared by solvent casting (by using acetone).

A glass substrate was used as standard, since its surface is considered hydrophilic ($\theta$ angle ~20-30º) [28].

The static contact angles obtained are presented in Table 3. The results suggest that the copolymers prepared are hydrophilic being the variation of contact angle due to incorporation of POSS residual.

![Fig. 3 – $^1$H-NMR spectrum of the POSS_0 and POSS_15 hybrid copolymers.](image)

![Fig. 4 – $^1$H-NMR signals identification for the POSS_15 hybrid copolymer.](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\theta$ angle ± $\Delta $/(º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS_0</td>
<td>80.0 ± 3.2</td>
</tr>
<tr>
<td>POSS_15</td>
<td>88.6 ± 2.6</td>
</tr>
<tr>
<td>Glass substrate</td>
<td>20.1 ± 2.8</td>
</tr>
</tbody>
</table>
In order to understand the influence of the incorporation of the POSS in the hybrid systems, the surface energy was determined. The surface free energy was calculated based on the static contact angles obtained for several probe liquids by using the OWRK (Owens-Wendt-Rabel and Kaelble) model, which consider both the dispersive and polymer contributions [18].

The results obtained for the surface energy are presented in Table 4.

Table 4 – Results obtained for the total surface tension (γ), dispersive component (γd) and polar component (γp) of the hybrid copolymers prepared.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>γ± SD (mN/m)</th>
<th>γd ± SD (mN/m)</th>
<th>γp ± SD (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS_0</td>
<td>34.24 ± 3.41</td>
<td>2.38 ± 0.73</td>
<td>31.87 ± 3.33</td>
</tr>
<tr>
<td>POSS_15</td>
<td>17.56 ± 2.60</td>
<td>10.52 ± 1.67</td>
<td>7.04 ± 2.00</td>
</tr>
<tr>
<td>Glass substrate</td>
<td>100.92 ± 3.8</td>
<td>0.47 ± 0.23</td>
<td>100.46 ± 3.80</td>
</tr>
</tbody>
</table>

It is possible to observe that the incorporation of the POSS into the hybrid copolymer system decreases the surface energy, which is related with the increase of the dispersive component. This effect is very important in coatings for protective applications [29].

3.4. Thermal behaviour

The thermal stability of the hybrid copolymers prepared was evaluated by termogravimetric analysis (TGA). The results obtained to the POSS_0 and POSS_15 hybrid copolymers, are presented in the Fig. 5 and in Table 5.

The POSS_0 and POSS_15 prepared, show high thermal resistance (start to degrade only around 225 ºC), when compared with the conventional epoxy systems [30]. The POSS incorporation in the hybrid polymeric systems decreases the degradation temperature (406 ºC to ~400 ºC) but increases the thermal stability of the material (1st degradation: 1.5 % to 0.65%). This behavior could be related to the presence of the POSS cage into the system. The POSS cage is formed by Si-O-Si covalent bonds, which presents higher bond dissociation compared to the Si-O and C-C bonds [5, 31].

This fact confirms that the POSS monomer was successfully covalent bonded to the polymeric structure. The presence of the POSS cage in the polymeric structure acts as an internal filler which promotes the stability of the final material [31].

Fig. 5 – Overlap of the TGA curves for the hybrid copolymers (POSS_0 and POSS_15) and for the iBu-POSS monomer.

It is possible to observe that the incorporation of the POSS into the hybrid copolymer system decreases the surface energy, which is related with the increase of the dispersive component. This effect is very important in coatings for protective applications [29].

3.5. Coating performance evaluation

The hybrid copolymer formulations (POSS_0 and POSS_15) were mixed with the hardener. The two mixture were homogenized for 5–10 minutes.

The final bi-component paint was used to coat: a) glass- to test brightness (NP EN ISO 2813) [32] and drying time (ASTM D 1640) [33], b) metal- to test adhesion (NP EN ISO 2409) [34], impact resistance (NP EN ISO 6272) [35] and flexibility (ASTM D 522) [36] and c) Leneta charts- to test the yellowness and whiteness index (ASTM E 313) [37]. All the coated materials present standard sizes.

The main results obtained are presented in Table 6.

Table 5 – Results obtained for the termogravimetric analysis (TGA) of the hybrid copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st Mass loss</th>
<th>%</th>
<th>T_%/°C</th>
<th>2nd Mass loss</th>
<th>%</th>
<th>T_%/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>iBu-POSS</td>
<td>68.83%</td>
<td>241.00</td>
<td>30.63%</td>
<td>396.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POSS_0</td>
<td>1.51%</td>
<td>227.02</td>
<td>96.50%</td>
<td>406.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POSS_15</td>
<td>0.65%</td>
<td>232.31</td>
<td>97.81%</td>
<td>400.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The paints formulated with the hybrid copolymers present good dispersion, no agglomeration or phase separation, which indicates that the copolymers were compatible with the other components of the system. The viscosity of the paints increased due to the presence of the POSS cage structure in the copolymer. It is known that the presence of the POSS cage, a rigid structure that occupies a very large space into the polymeric structure, narrows the molecules mobility into the polymeric chain increasing the viscosity of the system. After spreading the paint on a glass surface the drying time was evaluated (superficial and complete drying). Both films have a total drying time around 2 hours, showing the occurrence of cross-linking reaction with the hardener. The paint gloss value obtained was very low, which could be related to the amorphous character of the hybrid copolymer. The higher impact resistance, flexibility and adhesion properties when the new coatings were applied on the metal could be related to the dense structure promoted by the hybrid copolymer, which has oxirane and siloxane moieties in the polymeric chain. In principle these components were observed, without forming agglomerates or phase separation. The coating formulation shows quick drying (2 hours), however such time is synonym of a short pot-life. These materials showed excellent mechanical properties, good adhesion, flexibility and impact resistance.

In conclusion, the results presented in this work suggest that the new hybrid copolymers have high potential as protective coatings, namely as anticorrosive coatings, fact that must be proved in the next phase of the work, already initiated.

REFERENCES


