Optimizing the Coverage Density of Functional Groups over SiO₂ Nanoparticles: Toward High-Resistant and Low-Friction Hybrid Powder Coatings

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ABSTRACT: Hybrid powder coatings (HPC) with low friction and high hardness enhance the sliding speed and allow interlocking or meshing products to slide effortlessly within each other, saving energy. In automobiles, they decrease fuel consumption and greenhouse gas emission. In the present work, a new insight of the key role played by the coverage density of triethoxyphenylsilane (TPS) grafted to SiO₂ nanoparticles over the friction coefficient, hardness, elastic modulus, and roughness of HPC is presented for the first time. In all cases, a very low amount (0.1 wt %) of functionalized or unfunctionalized SiO₂ nanoparticles were added to a powder-coating formulation based on polyester resin. HPC formulated with functionalized nanoparticles at a suitable coverage density (HPC−TPS3) exhibited significantly low friction coefficient (μ = 0.12), strong wear resistance (under dry sliding conditions at 1 and 5 N of load), low roughness (Rₚ = 3.5 nm), and high hardness and elastic modulus on the surface. We demonstrated that it is possible to tune the macroscopic properties by varying only the coverage density of TPS that is chemically attached to SiO₂ nanoparticles. Also, a physicochemical explanation was disclosed, wherein a hydrophilic−hydrophobic balance between −OH and phenyl groups was proposed. In all cases, the phenyl group allows the migration of functionalized nanoparticles through the polyester matrix, enhancing the hardness and elastic modulus on the surface. Thus, the functional nanomaterial design with tunable coverage density is a powerful tool to improve the physical and superficial properties of powder coatings using low amounts of nanomaterial.

1. INTRODUCTION

Hybrid powder coatings (HPC) are very attractive materials from a scientific and industrial point of view because of their easy processability, higher surface coverage, and high rate of reuses with energy saving. Furthermore, because they are solid powders (free of volatile organic compounds), they are considered environmentally respectful with a wide range of uses in office furniture, tools, windows, automobiles, and household appliances and as a barrier to prevent corrosion of metal structures.

Many efforts have been focused to obtain HPC with improved physical−chemical properties by means of nanoparticle addition of SiO₂, TiO₂, CaCO₃ or nanoclays into saturated or un-saturated polyester, carboxylated polyester, and polyester/epoxy. In particular, polyester resins used in HPC are solids, with carboxyl-terminal groups, which react with suitable cure agents, such as triglycidyl isocyanurate (TGIC) to obtain HPC with good mechanical and esthetic properties. Nonetheless, although the presence of neat or functionalized nanoparticles/nanofillers enhances the mechanical and adhesion properties, as well as reduces the wear rate and decreases the friction coefficient (μ) of coated samples, large amounts of nanoparticles must be used to achieve significant results; however, this strategy changes the flowability and as a consequence their melt viscosity. Particularly, scientific works regarding HPC based on carboxylated polyester resins and functionalized SiO₂ nanoparticles are scarce, for example: Mirabedini and Kiamanesh added 1, 2, and 3 wt % of commercial functionalized SiO₂ nanoparticles (R972, functionalized with dimethyldichlorosilane and HDK H30 functionalized with dimethyldimethoxysilane) to a powder coating formulation. The authors found that HDK H30 increased the hardness, tensile strength, and elastic modulus of the coatings because of the good chemical interactions between functionalized nanoparticles and the polymeric matrix. Puig et al. studied organo-modified amorphous silica particles (OSP) with trifunctional organosilane (alkyl-triethoxysilane) as an adhesion promoter in a polyester powder coating. The results show that OSP incorporation (1, 2.5, 3.5, and 4.5 wt %) leads to an improvement in their corrosion protection of the coatings, as well as in their adhesion properties up to 2.5 wt %.

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Concentrations beyond 2.5 wt % promote the formation of aggregates, leading to the detriment of mechanical and electrochemical performance.

Moreover, a suitable design of new nanofillers with multifunctional performance offering good dispersion into the polymeric matrix, without strong flowability changes and using small amounts of nanomaterial (<1 wt %), is highly demanded. Therefore, it is clear that despite the existing industrial and scientific interest, fundamental aspects regarding how the “graft density” or “coverage density” of functional SiO₂ nanoparticles affects the macroscopic properties of the coatings (frictions, roughness, etc.) have not been addressed yet. On this basis, some fundamental questions have not been answered, such as how is the coverage density (also known as graft density) of TPS onto SiO₂ nanoparticles tuned and how many groups are possible to chemically attach? What is the optimal concentration of functional groups that allows any chemical compatibility between the functional organic groups and the polymeric matrix?

Hence, the role of the coverage density or graft density of triethoxyphenylsilane (TPS) functional groups chemically attached on SiO₂ nanoparticles over the macroscopic properties of HPC is studied for the first time to offer some answers to the questions proposed previously. Several levels of graft density (Gφ) of TPS on SiO₂ nanoparticles were obtained, wherein a plateau of maximum functionalization was reached. Three kinds of Gφ were selected and “scaled-up” to produce 1 g of material. In all cases, 0.1 wt % of functionalized or neat SiO₂ nanoparticles was added to a powder coating formulation, to obtain a hybrid coating with enhanced physical properties. Herein, we find that the friction coefficient (using a load of 1 and 5 N), wear resistant, roughness, hardness and elastic modulus of HPC can be modulated by varying only the coverage density of TPS chemically attached to SiO₂ nanoparticles; and this coverage density can be modified controlling the amount of functionalizing agent added during the functionalization reaction. Also, a physicochemical explanation was disclosed, wherein a hydrophobic−hydrophobic balance between −OH and phenyl groups was proposed. In all cases, the phenyl group allows the migration of functionalized nanoparticles through the polyester matrix, enhancing the hardness and elastic modulus on the surface. Thus, we demonstrate that the functionalization of SiO₂ nanoparticles with a judicious amount of organic molecules is the best way to obtain new enhanced materials using very low amounts of functional filler (0.1 wt %).

2. RESULTS AND DISCUSSION

2.1. Functionalization Mechanism of NPSiO₂ with TPS. The covalent grafting of alkoxysilane coupling agents (well-known as silylation reaction) has been carried out typically in aqueous solutions by a sequential hydrolysis/condensation reaction, wherein the activation of the surface by inorganic acids or using acidic aqueous solutions is necessary to improve the grafting process (e.g., sol−gel). Nonetheless, it is poorly reproducible and is a non-homogeneous process, because it produces an island-type grafting due to condensation and clustering of the alkoxysilane agents; furthermore, water is formed as a by-product affecting the chemical equilibrium, because the condensation rate reaction begins to dominate over the hydrolysis reaction. To avoid this, herein we performed the silylation reaction without any catalyst under anhydrous conditions using toluene as the nonpolar solvent. These reaction conditions promote excellent reproducibility and a uniform distribution of grafts (similar to those obtained during controlled vapor deposition). Figure 1 shows a schematic representation of the silylation reaction of NPSiO₂ with TPS under anhydrous conditions and nitrogen atmosphere at 60 °C.

Figure 1 shows the schematic silylation mechanism wherein the coupling mechanism consists of combined nucleophilic substitutions at the silicon atoms of both surface siloxane and silylating agent. Following Figure 1, first the nucleophilic attack is favored through bonding electron delocalization induced through a concerted nucleophilic attack of a silicon atom of the siloxane group by the oxygen atom of the ethoxy group because electron donor ability of oxygen decreases in the order C−O−C > C−O−Si > Si−O−Si. In this case, alkoxysilane moieties and the ethoxy group were chemically anchored to a silicon atom of siloxane, forming a new Si−O−Si bond and Si−OEt, respectively. After that, a second nucleophilic substitution occurs when a neighboring oxygen atom of the silanol group attacks the silicon atom of the alkoxysilane, which leads to a new Si−O−Si bond and ethanol as a by-product. Thus, a covalent attachment of alkoxysilane to the surface is achieved, wherein the phenyl group is considered a “hanging group” from the silica surface, which imparts the desired functionality.

Besides, it is well known that the mechanism of silylation in the presence of toluene anhydrous (no polar solvent) is nucleophilic (because in the presence of aqueous solution it is electrophilic) and as a consequence the graft takes place mainly on the hydrophobic portion of the silica surface (siloxane groups) and to a lesser extent over the hydrophilic portion (free silanols), as it will be demonstrated by Fourier transform infrared (FTIR) in another section of this paper. Furthermore, the stoichiometry of surface reactions with several alkoxysilanes (RSiX₃, R₂SiX₂, R₃SiX), wherein X = Cl, OCH₃ or OC₂H₅ and R = organic group, has been extensively studied, and also, it has been well established that using bifunctional (R₂SiX₂) or trifunctional (RSiX₃) alkoxysilanes to modify any...
surface, one of two Si–X groups per bonded functional group remain unreacted as shown in Figure 1.

2.2. ATR–FTIR Qualitative Evidence of NPSiO2 Functionalized with TPS. Alkoxysilane (TPS), neat NPSiO2 (without functionalization), and functionalized surface of NPSiO2 with different amounts of alkoxysilane (FSiO2–TPSX1−X=1,...,5) were characterized by attenuated total reflectance (ATR)–FTIR, and their spectra are shown in Figure 2.

Figure 2 shows characteristic vibrations corresponding to TPS: C–H stretching (ν(C–H) 3072–3029 cm−1) corresponding to the aromatic or unsaturated C(sp2)–H and out-of-plane ring C=C bending at 700 cm−1. Aliphatic: C–H 2975 cm−1 νs(CH3) 2887 cm−1 νs(CH2) 2927 cm−1 νas(CH2) 1391 cm−1 δs(CH2) 786 cm−1 δs(CH) out-of-plane. Symmetric and asymmetric stretching vibrations at 1079 and 1295 cm−1, respectively, were observed and attributed to C–O–Si. NPSiO2 exhibited a broad intermolecular hydrogen bond centered at 3387 cm−1 corresponding to silanol (Si–OH) groups. At 503, 786 cm−1, and in the region of 830–1200 cm−1 a very strong vibration attributed to stretching vibrations of Si–O–Si bonds was observed.

Indeed, as can be seen in Figure 2, the graft density increases with the alkoxysilane content fed. In all functionalized materials, C–H stretching at 3011 cm−1 corresponding to unsaturated C(sp2)–H (from TPS) was observed. Overtones or combination bands in the range of 2000–1600 cm−1 corresponding to the aromatic ring were identified in NPSiO2 functionalized, indicating the presence of TPS. Undeniably, all these vibrations are more evident when a high graft density was obtained. Furthermore, aliphatic groups also were observed which is in good agreement with the silylation mechanism showed in Figure 1, wherein ethoxy groups of the TPS molecule were chemically attached to the NPSiO2 surface and some of them did not participate in the silylation reaction.

Interestingly, as the graft density increased, the broadband at 1103 cm−1 corresponding to siloxane groups (Si–O–Si) of NPSiO2 was divided into two well-defined bands: at 1227 and 1064 cm−1. The first band (1227 cm−1) was attributed to the new covalent bonds Si–O–Si formed by (i) the reaction between siloxane groups from the silica surface and Si–OEt from alkoxysilane during the silylation reaction, and (ii) the subsequent reaction between Si–OH and Si–OEt (see the mechanism in Figure 1). The second band at 1064 cm−1 was attributed to unreacted Si–O–Si groups from the silica surface. Also, the intensity of bending vibrations of Si–O–Si at 808 and 503 cm−1 decreased notoriously when a high amount of alkoxysilane was used. This fact is in good agreement with the reaction mechanism showed before and it is confirmed that the graft takes place mainly on the hydrophobic portion (siloxane groups) of the silica surface as was mentioned previously.

2.3. Graft Density Analysis of NPSiO2 Functionalized with TPS. Thermogravimetric analysis (TGA) was used to analyze pure and functionalized NPSiO2 with different graft density of alkoxysilane (FSiO2–TPSX1−X=1,...,5) in order to obtain more understanding about: (i) the silylation reaction, (ii) the optimal graft density (Gφ), and (iii) the grafting yield (Gy) behavior. First, #OH/nm² on the NPSiO2 surface was calculated (using eq 6, see the Experimental Section) to be 2.8 OH/nm². This value is consistent with values reported by Mueller et al. for the same kind of NPSiO2 (A200) measured using TGA coupled with a mass spectrometer (TGA/MS). Also, here we propose a simple way to calculate the #OH/nm² as follows

$$\frac{\text{#OH}}{\text{nm}^2} = \frac{(\text{wt}_\text{eq} - \text{wt}_\text{800}) \times N_A}{M_{\text{H}_2\text{O}} \times \text{S}_{\text{spec}} \times \text{wt}_\text{i}} \times 10^{-18}$$

where wt is the initial sample weight before running TGA. Thus, using eq 1, we obtain 2.75 OH/nm² in concordance with the result obtained previously using eq 6. On the other hand, functionalization of dry NPSiO2 by reacting TPS alkoxysilane coupling agent can be easily carried out in toluene to give a monolayer, although for some alkoxysilanes possessing reactive groups, multilayers can be built up by repeated reactions between 2 alkoxysilane molecules and two previously chemisorbed layers. During the functionalization reaction, a molar excess of alkoxysilane has been employed in order to achieve the maximum coverage or maximum Gφ which is shown as a plateau level in Figure 3.

In Figure 3, graft density increases and grafting yield decreases as a function of the alkoxysilane concentration.
Consequently, as the alkoxysilane content increases the full saturation or maximum coverage of the nanoparticles surface is gradually reached, which is evidenced when no perceptible changes in the graft density value are observed. In this case, saturation of the nanoparticle surface by TPS was reached when a plateau level was obtained at $G_g = 0.79 \mu$mol/m$^2$ (0.47 molecules/nm$^2$) using $[\text{TPS}]_0 = 18 \mu$mol/m$^3$. This $G_g$ value (0.79 $\mu$mol/m$^2$) is lower than those values reported in the literature when trialkoxysilane or chlorosilane coupling agents have been used.\textsuperscript{1,4,16,17} Nevertheless, the surface coverage value depends strongly on both the alkoxysilane molar composition and the functional group structure. Also, it has been reported that alkoxysilane possessing one phenyl group attached to the silicon atom in their structure significantly decreases the surface coverage in a factor of 2.\textsuperscript{14} In the present contribution, the fact to obtain a plateau level reveals the full coverage of the nanoparticle surface by TPS; although this only represents 17.2% of Si atoms from the grafting density of functional groups labeled as $f$.\textsuperscript{14} This proper surface coverage value was obtained when trialkoxysilane or chlorosilane coupling agents have been used.\textsuperscript{11} As revealed in Table 1, different levels of $G_g$ for each kind of functionalized nanoparticles (FSiO$_2$−TPS$\chi$=1−5) were obtained from $G_g = 0.36 \mu$mol/m$^2$ ($f = 7.8\%$) up to reach the saturation at $G_g = 0.79 \mu$mol/m$^2$ ($f = 17.2\%$). According to these results, three kinds of functionalized nanoparticles with different density of functional groups labeled as FSiO$_2$−TPS1 (low $G_g$, $f = 7.8\%$), FSiO$_2$−TPS3 (medium $G_g$, $f = 11.4\%$), and FSiO$_2$−TPS5 (high $G_g$, $f = 17.2\%$) were chosen to be added to a powder coating formulation. Therefore, 5 g of each selected functionalized material (FSiO$_2$−TPS$\chi$=1,3,5) was obtained under the same procedure to produce 1 g of functionalized material, with the aiming to produce enough quantity of functionalized nanoparticles in order to be incorporated into a powder coating formulation and then to study the $G_g$ effect over their macroscopic properties. All "scaled up" functional materials exhibited the same $G_{\phi 1}$, $G_{\phi 2}$, and $f$ that those obtained using 1 g NPSiO$_2$ confirming thus the excellent reproducibility of the silylation reaction without a catalyst under anhydrous conditions.

### 2.4. HPC Formulations Based on Polymer/Nanoparticles

As was described in the Experimental Section, functionalized NPSiO$_2$ with TPS produced here "at large scale" (FSiO$_2$−TPS$\chi$=1,3,5), pure NPSiO$_2$, and R972 were added (0.1 wt % in each case) into a powder coating formulation based on polyester resin/TGIC/degassing and flowing agents (99.9 wt %). HPC formulations obtained here (HPC−TPS$\chi$=1,3,5, HPC−A200, HPC−R972) and control sample (PC, without nanoparticles) were characterized by differential scanning calorimetry (DSC), wherein two significant events as revealed in Figure 4 were observed.

![Figure 4](tag) Glass transition temperature ($T_g$) and cross-linking temperature ($T_{crosslinking}$) of HPC (HPC−TPS$\chi$=1,3,5, HPC−A200, HPC−R972) and control sample (PC, without nanoparticles).

The glass transition temperature ($T_g$) of powder coating formulation without nanoparticles (PC) was observed at 58.49 °C as well as an exothermic event at 179.3 °C ($AH = 10.1 \ J/\ g$). This latter was attributed to cross-linking temperature ($T_{crosslinking}$), which is due to the cure reaction between the carboxy groups from the end of polyester chains and the epoxy groups from TGIC, as was described by Piazza et al.\textsuperscript{11} Interestingly, a decrement of $\sim$1.7−2 °C on the $T_g$ of HPC−TPS$\chi$=1,3,5 was produced when FSiO$_2$−TPS$\chi$=1,3,5 were added (0.1 wt %) to the powder coating formulation, respectively. Herein, we propose that this decrement on the $T_g$ could be associated with a suitable dispersion of nanoparticles into the polymer matrix.\textsuperscript{11} This proper surface

### Table 1. TGA Analysis of NPSiO$_2$ Grafted with Different Amounts of TPS

| TAG       | $\mu$mol/m$^2$ | $\mu$mol/m$^2$ | molecules/nm$^2$ | $\%$ | $\%$
|-----------|----------------|----------------|-----------------|------|------
| NPSiO$_2$ | 1.25           | 0.36           | 9.3             | 28.4 | 7.8
| FSiO$_2$−TPS1 | 4.54           | 0.42           | 9.3             | 9.3  | 9.3
| FSiO$_2$−TPS3 | 9.07           | 0.52           | 9.3             | 5.7  | 11.4
| FSiO$_2$−TPS4 | 13.3           | 0.78           | 9.3             | 5.8  | 17.0
| FSiO$_2$−TPS5 | 18.0           | 0.79           | 9.3             | 4.4  | 17.2

*Is the initial alkoxysilane molar concentration in the feed per unit area of silica surface in $\mu$mol/m$^2$. $G_{\phi 1}$ (molecules/nm$^2$) was calculated using eq 1. $G_{\phi 2}$ was calculated using eq 5 (see Experimental Section). $f$ (%) = ($G_{\phi 2}/G_g$) × 100.
segregation of nanoparticles can produce a “plasticization effect” due to (i) the good interfacial interaction between the polyester matrix and the phenyl group (from TPS) and (ii) the additional free volume provided by the “plasticizer” (nanoparticle + functional segment), facilitating thus the segmental movements in the polymer chains, which promote a T_g reduction. Also, for all HPC–TPS(X)_1,3,5, the cross-linking enthalpy was practically the same (ΔH = 16.1, 15.8, 16 J/g) but not their T_crosslinking. In this sense, HPC–TPS1 (low G_p) exhibited a cure temperature of 185.8 °C, which represents an increase of 6.5 °C in comparison with the cure temperature of the control sample (PC = 179.3 °C). Furthermore, we observed that as the G_p increases, the T_crosslinking diminished up to 181.7 °C (high G_p). This phenomenon can be equivalent to increasing the amount of nanofiller added to a polymeric matrix; meanwhile in our case, we only systematically increase the number of functional groups (coverage density or G_p) maintaining fixed the total amount of nanoparticles added (0.1 wt %) to the powder coating formulation. This result is a clear evidence that modulating the coverage density can induce a significant change on the thermal macroscopic properties of powder coatings formulations. On the other hand, when pure NPSiO2 (A200) or R972 was added (0.1 wt %) to the powder coating formulation to obtain HPC-A200 and HPC-R972, respectively, and a slight increase of around 1 °C (respect to PC) on the T_g was observed. NPSiO2 (A200) and R972 possess hydroxyl and dimethyl groups on their surface, respectively. In both cases, these functional groups can promote nanoparticles agglomeration because of their high incompatibility with the polymer matrix, resulting in an increase in the powder coating stiffness.

2.5. Tribological Properties of HPC Electrostatically Deposited onto Carbon Steel Sheets. Each HPC (HPC–TPS(X)_1,3,5, HPC-A200, HPC-R972) as well as the control sample (PC) were electrostatically deposited onto carbon steel sheets and thermally cured to obtain a homogeneous film. The typical tribological curves of hybrid coatings at two normal loads of 1 and 5 N during 25 000 and 12 500 sliding cycles are given in Figure 5A,B, respectively. In Figure 5A, all hybrid coatings (HPC–TPS(X)_1,3,5, HPC-A200, HPC-R972) and control sample (PC, without nanoparticles) were subjected to a normal load of 1 N to assess their corresponding friction coefficient (μ). In all cases (except in PC), the content of nanoparticles was 0.1 wt %. The control sample PC exhibited a μ ≈ 0.15 during the first 18 000 sliding cycles; after that, the μ increased suddenly until an approximate value of μ ≈ 0.43. This abrupt increase is due to that during the tribological analysis (using a ball-on-disc tribometer, under dry-sliding conditions), the ball quickly wore-out the coating, exposing thus the coating–substrate interface as revealed in Figure 6B, which shows the wear tracks observed on the hybrid coating using an optical microscope. The wear rate (mm^3/Nm) and the volume lost (mm^3) also are shown in Figure 6A.

Hybrid coatings HPC-A200 and HPC-R972 in Figure 5A failed since the beginning of the tribological test, showing the highest value of μ ≈ 0.47. In this case, we propose that the presence of −OH groups (from A200) and −CH3 (from R972) promoted a poor dispersion, an unfavorable compatibility, and the presence of agglomerations. These latter produce big and fitful lumps on the surface of the coating, which are worn-out together with the adjacent polymeric matrix due to the abrasive wear by the steel ball. This deeper

Figure 5. Curves of friction coefficient (μ) vs sliding cycles for hybrid coatings (HPC–TPS(X)_1,3,5, HPC-A200, HPC-R972) and control sample (PC, without nanoparticles): (A) measured under an applied force of 1 N during 25 000 sliding cycles. (B) measured under an applied force of 5 N during 12 500 sliding cycles. In all cases, sliding speed was of 0.05 m/s.

Figure 6. Hybrid coatings (HPC–TPS(X)_1,3,5, HPC-A200, HPC-R972) and control sample (PC, without nanoparticles): (A) curves of volume lost (mm^3) and wear rate (mm^3/Nm) measured under an applied force of 1 and 5 N during 500 m. (B) Wear tracks observed for each sample using an optical microscope.
penetration in the hybrid coating is clearly observed by the wear tracks in Figure 6B. The fast wear rate at the beginning of the test is due to the lack of cohesive strength in the hybrid coatings HPC-A200 and HPC-R972.

Interestingly, very different tribological behaviors were observed by only tuning the coverage density of TPS (graft density, $G_{\phi} = 0.36, 0.52,$ and $0.79 \text{ } \mu \text{mol/nm}^2$) over the silica nanoparticles using functional hybrid coatings (HPC−TPS$|_{X=1,3,5}$). Thus, tribological performance corresponding to the HPC−TPS1 sample was similar to that observed in the control sample. In this case, FSiO$_2$−TPS1 (low $G_{\phi} = 0.36 \text{ } \mu \text{mol/nm}^2$ of TPS) was used, wherein some −OH groups were functionalized with TPS; however, this low coverage density seems to be enough to promote a similar performance to the control sample. Nevertheless, if silica nanoparticles are not functionalized or the functional groups are incompatible with the matrix, the tribological test fails quickly as was discussed previously.

When a high $G_{\phi} = 0.79 \text{ } \mu \text{mol/nm}^2$ of TPS is used to obtain HPC−TPS5, the friction coefficient progressively increases from $\mu \approx 0.13$ to $\mu \approx 0.15$ during the first 10,000 sliding cycles; after that, the coating fails reaching $\mu \approx 0.45$. Here, the maximum coverage of NPSiO$_2$ by TPS was obtained; and this high density of groups produces a good interaction (chemical affinity) between them, producing agglomeration of nanoparticles. This coalescence due to the presence of highly functionalized nanoparticles prevents their effective dispersion within the coating, which affects their tribological performance. In all cases, fluctuations in the friction curve were observed, which indicate a stick-slip behavior.

Good compatibility between the inorganic filler and the polymer matrix is highly desirable to improve the macroscopic properties of any composite. In the case of HPC−TPS3, an optimum graft density ($G_{\phi} = 0.52 \text{ } \mu \text{mol/nm}^2$) or coverage density was obtained. The suitable balance between −OH groups unfunctionalized and functional groups of TPS (phenyl groups in TPS are of the same nature that the polymeric matrix) suggests a good dispersion of FSiO$_2$−TPS3 within the coating, which improves the compatibility with the polymeric matrix and promotes a positive effect on the toughness of the polymer coating. Surprisingly, the wear track in this sample was not possible to observe under the optical microscope, as the volume lost during all test round was $1 \times 10^{-4} \text{ mm}^3$ (see Figure 6). Figure 5A shows the lowest friction coefficient obtained here of about $\mu \approx 0.12$ during all tribological tests (500 m, 25,000 sliding cycles). Also, the fluctuation associated with the stick-slip behavior was noticeably minimized.

On the other hand, when the load is increased up to 5 N (see Figure 5B), the control sample (PC) and hybrid coatings (HPC−TPS1, HPC−TPS5, HPC-A200, and HPC-R972) failed at the beginning of the tribological test. Indeed, the friction, wear tracks, and the amount of wear debris increased as increasing normal load, which is in good agreement with the Archard’s wear law. Nonetheless, the hybrid coating HPC−TPS3 exhibited a good wear resistance, maintaining a $\mu \approx 0.15$ during 12,500 sliding cycles. These results suggest that the surface of HPC−TPS3 ($G_{\phi} = 0.52 \text{ } \mu \text{mol/nm}^2$) is hard and strong with a flat topography without lumps (see AFM analysis).

2.6. Surface Analysis by AFM. As was described previously, the sample HPC−TPS3 ($G_{\phi} = 0.52 \text{ } \mu \text{mol/nm}^2$) exhibited the lowest friction coefficient at 1 and 5 N of nominal load. We believe that the functionalized nanoparticles (at this suitable graft density) promote a good dispersion in all surfaces, which enhances the surface hardness. This is due to the mechanical interlocking phenomenon between the func-
tional group (TPS) in the SiO$_2$ nanoparticles and the polymer; thus, the surface roughness (root mean square, $R_q$, also called rms) noticeably decreases as is shown in Figure 7.

In the case of HPC, HPC-A200 and HPC-R972, the polymer matrix does not interact with the functional groups on the surface of A200 (−OH) or R-972 (−CH$_3$). These chemical groups are incompatible with the polymer matrix, leading to large particle agglomerates as a consequence of the close contact between aggregates. This phenomenon is translated into a sharp topography with high $R_q$ values: 31.2 and 26.6 nm, respectively, with a low tribological performance and a high friction coefficient. On the other hand, PC (control sample) and HPC−TPS1 exhibited the same surface roughness $R_q = 10.3$ nm. This result is in good agreement with the evolution of the friction coefficient observed for the same samples during the tribological test (see Figure 5). In this case, HPC−TPS1 does not promote any changes in the surface roughness, because FSiO$_2$−TPS1 exhibited a low graft density ($G_g = 0.36$ μmol/nm$^2$) with a functionalization efficiency of 7.8%, which means that there exists many available −OH groups on the NPSiO$_2$ surface and/or a lot of NPSiO$_2$ unfunctionalized. Nevertheless, when densely covered nanoparticles ($G_g = 0.79$ μmol/nm$^2$) by TPS are used (wherein a “plateau” of maxima functionalization was obtained using large amounts of TPS: 18 μmol/nm$^2$) to obtain HPC−TPSS5, the surface roughness exhibited a slight decrease up to reach $R_q = 8$ nm. Nonetheless, this decrease in the roughness does not promote a surface with a low friction coefficient during all tests, as was disclosed before. It is due to the high density of TPS groups onto the nanoparticles (or low amount of −OH groups unfunctionalized), which produces a good chemical affinity between TPS groups and as a consequence their agglomeration. In perspective, this effect is similar when the −OH groups predominate over the TPS groups in the HPC−TPS1 sample. Interestingly, using a medium-functionalized material (FSiO$_2$−TPS3 with $G_g = 0.52$ μmol/nm$^2$), a good “balance” between −OH and TPS groups (HPC−TPS3, case) can promote a coating with enhanced macroscopic properties: low friction coefficient ($\mu \approx 0.12−0.14$ during all dry tribological test at 1 and 5 N), high Young modulus and hardness, and low roughness ($R_q = 3.5$ nm), as shown in Figure 7.

2.7. Mechanical Properties by Nano-indentation. On the basis of the surface roughness results and the frictional coefficient analysis of each system, we can correlate these two parameters as shown in Figure 8A, wherein the HPC−TPS3 exhibited the lowest both roughness (3.5 nm) and friction coefficient ($\mu \approx 0.12−0.14$) corresponding to a load of 1 and 5 N, respectively.

In general, we can affirm that the low roughness is contributed to the friction coefficient reduction as no micro-structured or textured surfaces were observed by AFM. On the other hand, the high wear resistant exhibited by HPC−TPS3 should be related to the specific hardness on the surface. In order to analyze this important issue, both the hardness and Young modulus of HPC (HPC−TPS$X|X=1,3,5$) and the control sample (PC, without nanoparticles) were obtained by nano-indentation on the cross section of each sample (depth profile with 10 nano-indentations per sample) as is schematized in Figure 8B. “0” position means hardness and elastic modulus measurements onto the solid–gas (outer coating-air) interface, and “10” position means hardness and elastic modulus measurements onto the solid–solid (inner coating–metallic substrate) interface. Between them (0–10), we measure 8 nano-indentation to scanning the transverse direction on the powder coating.
As shown in Figure 8C,D, the PC mechanical properties (hardness and Young modulus) were constant through the cross section of the powder coating. Certainly, this behavior is expected because the PC does not have any nanomaterial in its formulation, preserving their same mechanical properties through their thickness. Interestingly, HPC−TPS3 exhibited both the greater hardness (350 ± 10 MPa) and the highest Young modulus (10.1 ± 0.5) GPa onto the outer cross-sectional surface. In all hybrid materials, the hardness and the elastic modulus values decreased as the nano-indentation analysis progressed transversely through the coating, until reaching an average value located near to the coating center (depth: 40 μm). After that, the mechanical properties observed at more depth, increased slightly until to reach the solid−solid interface (depth: 80 μm). This behavior suggests the presence of a migration phenomenon of nanoparticles through the powder coating toward the interfaces as is schematized in Figure 9A−C.

Nanoparticle migration could be produced during the melting process before curing and was attributed to the suitable concentration of phenyl groups chemically attached to the silica nanoparticles, which are compatible with the polyester resin (bulk). As shown in Figure 9B, using nanoparticles with medium coverage density (HPC−TPS3, case), a good hydrophobic−hydrophilic balance between phenyl groups and −OH, respectively, was produced. Functionalized nanoparticles possess the suitable amount of phenyl groups per nm² like to promote their good dispersion into the polyester matrix, avoiding thus their agglomeration. Consequently, functionalized nanoparticles can migrate easily through the polymer to the top surface, enhancing the surface hardness (350 MPa), Young modulus (10 GPa), and it also promotes a low roughness (3 nm) and low superficial energy (28 mJ/m², measured by using a goniometer and using the Owens−Wendt−Rabel and Kaelble equation).

Meanwhile, in Figure 9A,C when functionalized nanoparticles with a low graft density were used (HPC−TPS1 case, many available −OH groups without reacting and/or several unfunctionalized nanoparticles), or in the opposite case, when functionalized nanoparticles with a high graft density were used (HPC−TPS5 case, a lot of phenyl groups chemically attached to the NPSiO₂ but some −OH unfunctionalized), the hydrophobic−hydrophilic balance between phenyl groups and −OH was lost. Thus, the high density of −OH groups (HPC−TPS1 case) or phenyl groups (HPC−TPS5 case) onto the nanoparticle surface promotes in both cases their agglomeration by the chemical affinity between −OH groups or between phenyl groups. Nonetheless, the presence of phenyl groups promotes the migration of these agglomerates to the coating surface, propitiating a very rough surface, a high specific surface energy, a high friction coefficient, but with a slight improvement in the hardness and Young modulus in the top-coating.

Finally, the interaction between 100Cr6 balls and the HPC surfaces (HPC−TPSₓ (x=1,3,5)) was analyzed. Figure 9D,F shows scanning electron microscopy (SEM) micrographs corresponding to the 100Cr6 ball after the tribological test for the samples HPC−TPS1 and HPC−TPS5, respectively. In both cases, coatings debris surrounding the contact surface of the ball were observed, which is consistent with the hardness and the roughness obtained by AFM analysis. These surfaces exhibited a sharp topology with several lumps that can be breaking or wearing by the action of the load on the ball. Also, a film transfer on the ball in both cases was not observed. An SEM micrograph corresponding to the 100Cr6 ball after the tribological test to the sample HPC−TPS3 is shown in Figure 9E. In this case, does not debris was observed on the contact surface around the ball, neither does the presence of a film-transfer that could reduce the friction coefficient.

3. CONCLUSIONS

On the basis of the aforementioned discussion in the previous section, it could be concluded that a deeper insight regarding how the graft density (Gₓ) of TPS groups onto NPSiO₂ affects the macroscopic properties of HPC is offered for the first time. Here, several graft densities or coverage density (from 0.36 up to 0.79 μmol/nm²) of NPSiO₂ with TPS were obtained by varying the amount of TPS (1.25, 4.54, 9.07, 13.3 and 18.0 μmol/m²) used in the functionalization reaction of NPSiO₂ under a nucleophilic substitution mechanism and anhydrous conditions. A "plateau" of maxima functionalization was reached using 13.3 μmol/m² of TPS. HPC formulated with functionalized nanoparticles at a suitable coverage density (Gₓ ≈ 0.52 μmol/nm², HPC−TPS3 case) exhibited significantly low friction coefficient (μ = 0.12), strong wear resistance (under dry sliding conditions at 1 and 5 N of load), low...
roughness \( R_q = 3.5 \text{ nm} \), and high hardness and elastic modulus on the surface. We demonstrated that it is possible to tune the macroscopic properties by varying only the coverage density of TPS that is chemically attached to \( \text{SiO}_2 \) nanoparticles. Also, a physicochemical explanation was disclosed, wherein a hydrophilic–hydrophobic balance between \(-OH\) and phenyl groups was proposed. In all cases, the phenyl group allows the migration of functionalized nanoparticles through the polyester matrix, enhancing the hardness and elastic modulus on the surface. Thus, the functional nanomaterial design with tunable coverage density is a powerful tool to improve the physical and superficial properties of powder coatings using low amounts of nanomaterial.

4. EXPERIMENTAL SECTION

4.1. Materials. Silica nanoparticles (NPSiO\(_2\), AEROSIL A200, Evonik, \( \sigma = 12 \text{ nm} \), 2.75 OH groups/nm\(^2\)) and a specific surface area 201 m\(^2\)/g (measured by Brunauer–Emmett–Teller, BET) was dried during 4 h at 150 °C under vacuum before use, in order to remove the physically adsorbed water. Hydrophobic-fumed silica AEROSIL R972 (fumed silica after being treated with dimethyldichlorosilane) from Evonik, \( \sigma = 16 \text{ nm} \), and BET = 127 m\(^2\)/g. Toluene anhydrous (99.8 % Aldrich), TPS (98 % Aldrich, \( M_w = 240.37 \text{ g/mol} \)), methanol (CH\(_3\)OH, 99.98 % T.J. Baker), polyester resin with carboxyl terminal groups (Sun Polymers International Inc.: \( T_G = 62 ^\circ \text{C} \), 25–40 mg KOH/g, \( M_w = 7680 \text{ Da} \), \( D_w = 1.39 \)) and T\( \gamma \)GIC (\( M_w = 7845 \text{ Da} \), \( D_w = 1.46 \), \( T_G = -1.84 ^\circ \text{C} \)) as cure agent were used as received.

4.2. Instrumentation. New functional groups chemically attached to the silica surface from FSiO\(_2\)–TPSX\(_{1-3,5}\) were analyzed by ATR using a Frontier MIR PerkinElmer ATR–FTIR spectrometer of 4000–400 cm\(^{-1}\) using 12 scans and 0.4 cm\(^{-1}\) of resolution at room temperature. Coverage density was calculated by TGA and was performed in a TA Instrument SDT Q600 system using alumina crucibles and heating from room temperature up to 900 °C at 10 °C/min under a feed of ultrahigh purity nitrogen gas (100 mL/min). Co-rotating twin screw extruder (L/D) = 40 at 120 rpm and 110 °C was used to obtain all formulations of HPC. Thermal characterization of formulations of HPC (HPC-A200, HPC-R972, HPC–TPSX\(_{1-3,5}\)) and control sample (PC, without nanoparticles) were analyzed by DSC in a TA Instruments DSC Q200 system. Typically, 1–2 mg of each sample was placed into an aluminum pan (Tzero) and under nitrogen \( 100 \text{ mL/min} \) were analyzed by DSC in a TA Instruments DSC Q200 system. Typically, 1–2 mg of each sample was placed into an aluminum pan (Tzero) and under nitrogen \( 100 \text{ mL/min} \) were subjected to the following thermal treatment: (1) a heating \( 10 ^\circ \text{C/min} \) from 0 °C up to 120 °C; (2) 120 °C isothermal for 1 min; (3) a cooling at 10 °C/min from 120 °C up to 0 °C; (4) 0 °C isothermal for 1 min; and (5) a heating at 10 °C/min over the range of 10 °C up to 300 °C. Thermal transitions were obtained in the second heating cycle when the polymer thermal history was eliminated. TGA was performed in a TA Instrument SDT Q600 system using platinum crucibles and heating from room temperature up to 800 °C at 10 °C/min under a feed of ultrahigh purity nitrogen gas (100 mL/min). Tribological performance of coatings under dry sliding condition was evaluated using a ball-on-disc tribometer (Anton Paar) under ambient conditions (relative humidity of 30–40%) using loads of 1 and 5 N and a sliding speed of 0.05 m/s and 100Cr6 balls of 6 mm of diameter as counterparts. The radius of the wear track was set to 7 mm and the sliding distance was 500 m. Friction force was dynamically measured and the friction coefficients were obtained when the measured forces were divided by the applied load. The wear coefficient of each sample was then calculated from the volume of material lost during the friction run using the following eqs 2 and 3:

\[
W_{\text{rate}} = \frac{V_{\text{lost}}}{F \times s}
\]

\[
V_{\text{lost}} = 2\pi R \left[ r^2 \sin^{-1}\left(\frac{d}{2r}\right) - \frac{d}{4} \left(4r^2d^2\right)^{0.5}\right]
\]

where \( W_{\text{rate}} \) is the wear rate coefficient, \( V_{\text{lost}} \) is the volume of material lost, \( F \) is the normal load, and \( s \) is the sliding distance. \( R \) and \( d \) are respectively the radius and width of the wear track and \( r \) is the radius of the steel-ball. The wear track on the ball was observed using a Scanning Electron Microscopy JEOl 6010 system. AFM (Asylum MFP 3D) was used to investigate the roughness of the coatings, which was correlated with the friction coefficients obtained. Noncontact (“tapping”) mode was used to obtain all topographic images using a rectangular cantilever AC160TS-35. Finally, nano-indentation experiments were carried out using a Hysitron TI950 Truboindenter (Hysitron Inc., Minneapolis USA) with 150 nm diamond Berkovik tip. The truboindenter was used in quasi-static indentation mode in order to measure the elastic modulus (Young modulus) and hardness of the hybrid powder coating cross-section.

4.3. Functionalization of NPSiO\(_2\) with TPS. Several levels of graft density \( \left( G_w \right) \) were obtained using 0.25, 0.91, 1.82, 2.67, and 3.61 mmol of TPS as revealed in Table 2.

| TAG | NPSiO\(_2\) (g) | triethoxysilylphenylethynyl (TPS) (g) | \((\text{mmol/m}^2)\)* |
|-----|----------------|-----------------------------------|---------------------|
| FSO\(_2\)–TPS1 | 1 | 0.06 | 1.25 |
| FSO\(_2\)–TPS2 | 1 | 0.22 | 4.54 |
| FSO\(_2\)–TPS3 | 1 | 0.44 | 9.07 |
| FSO\(_2\)–TPS4 | 1 | 0.64 | 13.3 |
| FSO\(_2\)–TPS5 | 1 | 0.87 | 18.0 |

*Is the initial alkoxysilane molar concentration in the feed per unit area of silica surface in \text{mmol/m}^2."

Thus, NPSiO\(_2\) A200 (1 g, previously dried) was placed into a jacketed glass reactor of 250 mL in the presence of anhydrous toluene (28.5 mL). The glass reactor equipped with addition funnel, condenser, and magnetic stirrer was sealed, purged with anhydrous nitrogen (15 min), and it was immersed in an ultrasonic bath (15 min) to enhance the nanoparticles dispersion. After that, the mixture was heated up to 60 °C, and then, the required amount of TPS dissolved in anhydrous toluene (1 g) was added dropwise. The functionalization reaction was stirred for 24 h at 60 °C. Functionalized NPSiO\(_2\) with TPS (FSiO\(_2\)–TPS) was isolated by vacuum filtration using a nylon membrane of 0.2 \mu m and were washed exhaustively with methanol (3 times) under vigorous stirring. Finally, FSiO\(_2\)–TPS nanoparticles were isolated and dried during 24 h using a vacuum oven at room temperature and were stored into a desiccator prior characterization. Thus, five kinds of functionalized NPSiO\(_2\) possessing different graft density \( \left( G_w \right) \) were obtained \( \text{FSiO}_2–\text{TPS}\_x\_y\_z\). Moreover, with the aim to have enough quantity of functionalized nanoparticles, we performed a second experimental set, wherein 5 g of FSiO\(_2\)–TPS1 (low \( G_w \)), FSiO\(_2\)–TPS3 (medium \( G_w \)), and FSiO\(_2\)–TPS5 (high \( G_w \)) were
obtained following the same procedure disclosed above. Each material with different graft density was later incorporated into a powder coating formulation.

4.4. Grafting Density Analysis. The graft density (\(G_p\)) or coverage density of TPS on the NPSiO\(_2\) surface (FSiO\(_2\)–TPS\(_{X=1-3,5}\)) was calculated by TGA using eq 3

\[
G_p (\text{\(\mu\)mol/m}^2) = \left(\frac{W_{\text{wet},800}}{100-W_{\text{wet},800}}\right) \times \frac{100 - (W_{\text{A200}})}{M_N \times S_{\text{spec}} \times 100} \times 10^6
\]

where \(W_{\text{A200}}\) is the weight loss of SiO\(_2\) nanoparticles (dihydroxylation) before functionalization and \(W_{\text{wet},800}\) is the weight loss between 60 and 800 °C corresponding to the thermal decomposition of TPS\(_{X=1-3,5}\). \(M_N\) is the molecular weight of the degradable part of the grafted TPS and \(S_{\text{spec}}\) is the specific surface area of NPSiO\(_2\) A200. Also, using \(G_p\) it is possible to obtain the grafting yield (\(G_y\)), which corresponds to the fraction of alkoxysilane (TPS) attached to the silica surface with respect to [TPS]_0

\[
G_y (%) = \frac{G_p \times 100}{[\text{TPS}]_0}
\]

where [TPS]_0 is the initial alkoxysilane molar concentration in the feed per unit area of silica surface in \(\mu\)mol/m\(^2\). On the other hand, according to Mueller et al.,\(^{18}\) it is feasible to obtain the OH surface density of pure NPSiO\(_2\) which can be calculated as follows

\[
\left(\frac{\# \text{OH}}{\text{nm}^2}\right) = \alpha \frac{\# \text{OH}_{800}}{\text{wt}_{800} \times S_{\text{spec}} \times \text{wt}_{800} + \frac{(\text{wt}_{800} - \text{wt}_{800}) \times N_A}{M_{\text{H,O}}}}
\]

where \(\text{wt}_{800}\) and \(\text{wt}_{800}\) represent the sample weights at the corresponding temperatures, \(M_{\text{H,O}}\) is Avogadro’s constant, \(\alpha = 0.625\) is a calibration factor,\(^{15}\) and \((\# \text{OH}/\text{nm}^2)_{800} = 1\) and represents the number of OH/\(\text{nm}^2\) remains on the NPSiO\(_2\) surface at 800 °C.\(^{21}\)

4.5. HPC Formulations. In order to study the graft density (\(G_y\)) effect over the macroscopic properties of the powder coatings resulting, we performed three hybrid powder coating formulations (HPC–TPS1, HPC–TPS3, and HPC–TPS5) based on (polyester resin/TGIC/degassing & flowing agents)/FSiO\(_2\)–TPS\(_{X=1-3,5}\) (99.9)/0.1 wt %. Furthermore, silica nanoparticles A200 and R972 also were used (instead of functionalized SiO\(_2\) nanoparticles) at the same weight content (0.1 wt %) in order to obtain hybrid powder coating formulations (HPC-A200 and HPC-R972) to make comparisons and to study trends. An additional powder coating formulation without nanoparticles (PC) as “control sample” also was done. In all cases, each powder coating formulation was homogenized using a high-power disperser, which produces a high shear force to disperse all components. The homogeneous powder dispersion was subsequently extruded to avoid premature curing of the system. The hotmelt materials were passed through cooled rollers in order to obtain hard, cool, and brittle flakes, which were broken into small flakes using a rotating hammer. The small flakes were then pulverized in a high-speed lab-mill and were sieved to obtain powder coating nanocomposites with a particle size of 30–35 \(\mu\)m.

4.6. Coatings Electrostatically Deposited on Carbon Steel. In all cases, control sample (PC) and HPC obtained here (HPC-A200, HPC-R972, and HPC–TPS\(_{X=1-3,5}\)) were applied onto carbon steel sheets (previously degreased) of 5 cm \(\times\) 10 cm (width and length) and 2 mm of thickness using a WAGNER electrostatic spray gun (output voltage of 60 kV). After that, the coated samples were cured for 15 min at 190 °C. The coated samples exhibited a homogenous thickness of 70 ± 6 \(\mu\)m (measured using an Elcometer 456 Coating Thickness Gauge instrument). Finally, all cured coating samples were characterized by AFM and tribology.

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