

Catalysis Research of PDMSUr-PWA Films: Aspects to be Considered

Orlando Elguera Ysnaga*

Institute of Chemistry of Sao Carlos, University of Sao Paulo (IQSC-USP), Sao Carlos-SP, Brazil

*Corresponding author:

Orlando Elguera Ysnaga

Institute of Chemistry of Sao Carlos, University of Sao Paulo (IQSC-USP), Sao Carlos-SP, Brazil

Email: orlandoelguera@gmail.com

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ABSTRACT

PU/PDMS based co-polymers present as drawbacks low hardness and tenacity. By this reason, they are reinforced with silicate structure like ormosil, which is acting as a reinforcement agent. In turn, these ormosil can act as a suitable matrix to host polyoxometalates like phosphotungstic acid ($H_3PW_{12}O_{40}$ / PWA). Thus, PDMSUr-PWA films (containing PDMS, Urethanes, Polyurethanes, Silicates and PWA), which constitute hybrid materials exhibit interesting mechanical and chemical properties, looking to satisfy part of the demand of thermal and electrical insulators and anticorrosive coatings also. For the applications of these materials are necessary the correlation among structure, composition, and properties. From results of XPS and ATR FT-MIR analysis constitute evidence of the presence of molecular ($[PW_{12}O_{40}]^{3-}$) and atomic (W) Tungsten at top Surface (10 nm of depth) of these materials. Furthermore, considering features that PDMSUr-PWA films exhibit e.g. elasticity and hardness, one can infer that these materials could constitute a structural support for PWA in applications of heterogeneous catalysis in many chemical reactions. PDMSUr-PWA film containing 35 w/w% of PWA approximately (content at which the W concentration is maxima), the Tungsten segregation at surface of these films is predominant. Additionally, if it is taken in consideration the significant Bromine presence at surface at the concentration of PWA mentioned above, one could deduct that this sample is candidate for application as anticorrosive coatings. Finally, taking advantage of the Proton conductivity of PWA, this sample also could be considered as a mixed conductor (of protons and electrons), which in the form of membranes fulfill the requirements in order to be used as fuel cells.

Keywords: PDMSUr-PWA films, Phosphotungstic acid ($H_3PW_{12}O_{40}$ / PWA), X-ray Photoelectron Spectrometry (XPS), Synchrotron Radiation (SR), Grazing Incidence X-ray Fluorescence (GIXRF)

INTRODUCTION

The investigations done about these hybrid materials (organo-inorganic phases linked by covalent bonds) from 2011 to 2015 in our research group, in conjunction with supporting additional former and later investigations referent to those years about materials based on Polyurethanes (PU)/Polydimethylsiloxane (PDMS) copolymers, in 2022 was published a Mini-review, in order to collaborate in the development of these new films, due to the varied properties and potential applications that they possess [1]:

- Photochromic and photocatalytic properties.
- Potential candidates as Proton exchange membrane fuel cells (PEMFCs).
- Potential candidates as polymeric biomaterials.

Polyurethanes (PU) are widely used as high-performance adhesives, coatings, and elastomers. Nonetheless, one limitation is their thermal stability that can be improved by insertion of poly (dimethylsiloxane) (PDMS) segments, which share their characteristics such as thermal stability (caused by the introduction of Si–O bonds), low surface energy, and water repellence, etc. [2]. Nevertheless, the poor mechanical properties of PDMS, e.g. abrasion resistance, thermal stability limit their application in many fields. This thermal stability could be improved by means of the incorporation of Silica nanoparticles and/or cross-linking agents [3-7]. However, PDMS is incompatible with PU, leading to the creation of a polymer phase thermodynamically and mechanically incompatible. Furthermore, PU/PDMS co-polymers present low hardness and tenacity. For this reason, reinforcing agents, compounds that forming cross-linked bonds/structures, like ormosil (Organically Modified Silicates), are needed in the PDMS/PU system in order to combine their properties [4,5]. One example of ormosil constitutes the use of amino-functionalized alkoxysilane, like 3-aminopropyltriethoxysilane (APTES) that improving the adhesion properties of these copolymers [4,5]. APTES allows the production of a Class II hybrid material (joined through of covalent bonds or intermolecular interactions) based in the chemistry of Sol-gel process, which constitutes a rapid method for fabrication of ceramics, glasses, and thin films [8]. A way to introduce PDMS segments and Silica contents in PU matrix is by means of the preparation of cyclic carbonates from an epoxydic reagent bearing PDMS, as was published by our research group [9-11]. Insertion of PDMS and Silica terminal groups in a unique oligomeric backbone

makes possible to obtain a hybrid polyurethane (PDMSUr) with valuable physical-chemical properties such as thermal resistance, hardness, corrosion protection, adhesion in glasses, besides others. PDMS–Silica Hybrids, consist of nm-sized Silica clusters and PDMS chains [10]. PDMSUr is suitable for use as anti-corrosive coatings, in which an important feature to consider is the hydrophobicity. This property (inherent in PDMS segments) prevents the corrosion and is dependent on the functional group (-CH₃, -CF₃, -OCH₃, -COOCH₃-, -Br) attached to the silicone chain. On another hand, the presence of polar functional groups such as -OH, -NH₂ or —COOH would increase the hydrogen bonding interactions, thus the polar characteristics of the surface energy [9-12]. The hybrid polyhydroxyurethanes PDMS-derived (PDMSUr) are materials that contain on its chemical backbone polydimethylsiloxane segments, and as end group, silicate or ormosil (Organically Modified Silica) regions [11]. Furthermore, ormosil as APTES constitutes a host network for polyoxometalates, such as phosphotungstic acid (PWA), which acts as reinforcing agent inside the hybrid material through of their crosslink structures. Sol-Gel process allows a better distribution of PWAs, and the control for size of the particles. PWA acts as a catalyst in the hydrolysis, condensation, and polycondensation reactions of this process, besides of providing other electrical and mechanical to properties to the material [11]. Heteropolyacid (PWA), in addition to behaving as the catalyst for Sol-gel reactions also provides other interesting properties to the final hybrid material, such as proton conductivity, increase in elastic modulus and hardness [12]. Thus, the final product consists of a hybrid urethanesil (PDMSUr) with PWA molecules incorporated into the matrix. Functional materials as PDMSUr-PWA films present easy processing, excellent toughness and durability. PDMSUr- PWA films also present hydrophobicity and non-hygroscopic properties, which makes potential candidates for high-performance adhesives, corrosion-resistant coatings for Steel and Titanium alloys surfaces in different media. The hydrophobicity (in which the PWA playing an important role also [9]), in the surface of PDMSUr-PWA films constitute a physical barrier in order to avoid corrosion of metals (as Ti6Al4V and SS316L) in different aggressive media (basic, saline and acidic). These materials exhibit hydrophilic and hydrophobic domains, which would favor their use as membranes for fuel cells, photochromic applications, smart windows, adhesives in laminated windows [11-13]. Electrostatic and Van der Waals forces on PDMSUr surfaces are among the interactions that influence the adhesion properties, which could be related with the hydrophilic characteristics based on the polar groups (e.g. hydroxyls: -OH, ether: R-O-R', and carboxyl: —COOH) at

surface, according to X-ray Photoelectron Spectroscopy (XPS) [12-14].

MATERIALS AND METHODS FOR THE PREPARATION AND ANALYSIS OF FILMS

Materials

All reagents used to synthesize the precursor cyclic carbonate PDMS-derived, here labelled as CCPDMS, are described in references [9-10]. To the obtaining of polyhydroxyurethanes PDMS-derived (PDMSUr), the following reactants were used: purified CCPDMS, 3-aminopropyltriethoxysilane (APTES, >98%, Sigma Aldrich), 3-aminomethyl-3,5,5-trimethylcyclohexylamine (IPDA, > 99%, mixture of cis and trans, Sigma Aldrich), dimethylacetamide (DMAc, 99,5%, Vetec), nitrogen (N₂, > 99%, White Martins), phosphotungstic acid hydrate (PWA, Sigma Aldrich) dried at 60°C overnight.

Method of Preparation of Films

The synthesis of the precursors CCPDMS followed the procedure described by Aguiar et al [8-9]. After purification of CCPDMS, 0.42 g (1 mmol) was mixed with 0.218 g (3 mmol) of APTES in a vial previously purged with N₂. The reaction mixture remained under stirring for 40 minutes at 70°C. Finally, the samples were dissolved in 2 mL of DMAc were dispersed into the hybrid polyurethane matrix and stirred for 24 h at 60°C [9-10].

Methods for the Analysis of Films

Infrared Spectroscopy

Mid-infrared spectroscopy (FTMIR): A BOMEM MB102 FTIR spectrometer was employed to analyze the formation of the cyclic carbonate group and urethanic bonds in the range 250–4000 cm⁻¹, 32 scans and instrumental resolution set at 4 cm⁻¹ in transmission mode (FTMIR-T) of analysis. The samples were cast on a Silicon wafer before the measurements. To carry on the quantitative analysis of CCPDMS by FTIR, a 25 µm thick Silicon wafer was used on Transmission FTIR measurements [10,11].

Attenuated total reflectance middle infrared spectroscopy (ATR-FT-MIR): Spectra were acquired using a Nicolet Nexus 470 spectrometer (range 650 cm⁻¹–4000 cm⁻¹, resolution 4 cm⁻¹, 64 scans; Thermo Fisher Scientific) equipped with a Zinc Selenide (ZnSe) crystal, operating in attenuated Total Reflectance (ATR) mode.

X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were taken using a Kratos Ultra system applying the following acquisition parameters: base pressure: 4.10⁻⁸ Pa, sample neutralization applying low energy electrons (< 5 eV), hybrid mode (electrostatic and magnetic lenses are used), take off angle of electrons 0°, pass energy 20 eV (or, respectively, 40 eV in case of some N1s spectra) in high resolution spectra and 160 eV in survey spectra, excitation of photoelectrons by monochromatic AlK α radiation. The area of analysis is elliptically shaped with main axes of 300 µm x 700 µm. The binding energy calibration of the electrically isolating polymer was performed by referring the C1s component of aliphatic carbon species to 285.0 eV. Binding energies are given with a precision of ± 0.1 eV throughout this contribution and peak widths are indicated as full width at half maximum (FWHM) with a precision of ± 0.05 eV. Elemental ratio was calculated based on the area of the peaks and considering the percentage of the elements provided by XPS [9,12].

Synchrotron Radiation Grazing Incidence X-ray Fluorescence (SR-GIXRF)

SR-GIXRF measurements were performed at the D09B (15°) bending-magnet XRF beamline of the Brazilian Synchrotron Light Source (LNLS, Campinas-Brazil) [13]. The experimental setup for SR-GIXRF analysis includes the 1.4 GeV source (storage ring); a monochromatic X-ray beam (beam size 0.1mm Vx5.0mm H), set at energy 11 keV for Tungsten determination; and a HPGe detector, cooled by N₂(l), operating in energy dispersion mode. The grazing angles range of SR-GIXRF measurements was 0.05°–0.2° [14].

DISCUSSION OF RESULTS

PDMSUr-PWA samples containing 1 w/w% PWA and 35 w/w% PWA were analyzed by FTIR and XPS (average depth 50 Å > 5 nm). The condensation of silanol groups in Sol–Gel process allows the formation of silicate regions, which are a host network for polyoxometalates [10,11]. PDMS segments are characterized by the presence of a doublet between 1100 cm⁻¹ and 1020 cm⁻¹, correspondent to symmetric and asymmetric stretching of the siloxane bonds Si–O–Si. FTIR spectrum of the PDMSUr-PWA sample containing 35 w/w% PWA showed absorption bands characteristic of the Keggin structure of PWA: 1080 cm⁻¹ [P–O_a], 984 cm⁻¹ [W=O_d], 889 cm⁻¹ [$\nu_{as}(W-O_b-W)$], and 802 cm⁻¹ [$\nu_s(W-O_c-W)$]. Thus, these features indicating the preservation of PWA molecules inside the films [11 and therein references]. The $\nu_{as}(W-O_b-W)$ absorption has shifted

to the blue region of the electromagnetic spectrum (from 889 cm^{-1} to 895 cm^{-1}). This finding can indicate interactions between Keggin ions and silicate regions, mainly through of silanol groups, and columbic interactions between the organic matrix and heteropolyanion. [11 and therein references].

Comparing the spectra of pure PWA bands with the corresponding Ormosil films, there is a shift of the W=O bond band towards lower wavenumbers [12, Figure 56]. This observation may indicate a strong interaction between Keggin ions and silicate regions. Protonated silanol ($\equiv\text{Si-OH}_2^+$) can act as a counter-ion for the polyanion (PWA) leading to the generation of ($\equiv\text{Si-OH}_2^+$)($\text{H}_2\text{PW}_{12}\text{O}_{40}^-$) ionic species. Another observation from the spectra mentioned above was the indication of the complete hydrolysis of the alkoxy silane (APTES). Thus, ATR FT-MIR analysis revealed that the molecular structure of PWA heteropolyacid maintained its Keggin structure inside of PDMSUr-PWA samples hybrid film, through interactions with the organic matrix PDMSUr or with silanol groups of the inorganic part (Ormosil) [12-p110, 15].

The XPS Silicon spectrum showed a clearly signal observed Si(2p) at binding energy of 102.3 eV is attributed to Silicone specie [11 and therein references]. Carbon XPS spectrum (at the region corresponding of atomic orbital C1s) were identified by four distinct peaks: one at 285 eV (C*-C); two peaks around 286-288 eV (C*-N, C*-OH alcohol and C*-O-C ether); and the peak with the highest binding energy (at 289 eV) interpreted as Carbon resulting from urethane species (-N-C*O-O-). Evaluating the Nitrogen XPS spectrum (at the region corresponding of atomic orbital N1s), two main species were identified, which can be attributed to the urethane bond at approximately 400 eV and to the positively charged Nitrogen species or interacting by hydrogen bonds, with binding energy between 401-402 eV. Evaluating the Tungsten XPS spectrum (W at the region corresponding of atomic orbital W4f) from phosphotungstate ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) was identified within the information range given by XPS (10 nm from the surface) in the PDMSUr-PWA films hybrid films containing 1%w/w of PWA and 35%w/w of PWA. The atomic percentage of Tungsten (W) in the samples containing 1% and 35% of PWA were around 0.1% and 2.3-2.7% respectively. The characteristic W4f doublet corresponding to $W4f_{5/2}$ and $W4f_{7/2}$ (separation between them of 2.1 eV), which is characteristic of the oxidation state W^{+6} was identified in the samples mentioned above at approximate binding energies of 38 eV and 36 eV, respectively. The PWA heteropolyacid could interact electrostatically with free amines or unreacted

amines, given the emergence of these protonated species, observed by XPS on the surface of the hybrid films. The XPS Oxygen spectrum (at the region corresponding of atomic orbital O1s) were found peaks at range of binding energies 537-527 eV, which can be assigned to the contributions from the WO*W, W=O*/C *=O /SiO*Si and CO*C groups [9,12].

From characterization and analyses of these hybrid materials was possible to conclude that at PWA concentrations less than 35 w/w% of PWA, the Tungsten segregation at surface of these films is predominant, based probably on the electrostatic interactions among PWA with ormosil and amine groups [12, 15]. There is segregation of Bromine at surface of PDMSUr- PWA films, which is function of PWA concentration. The presence of Bromine could contribute with their corresponding adhesive and anti-corrosive properties. The films containing 1%, 35%, 40-50% w/w of PWA would be suitable for anticorrosive coatings, based on the significant Bromine presence at surface. From Synchrotron Radiation Grazing Incidence X-ray fluorescence (SR-GIXRF) analysis, there are indicatives of segregation of Bromine at the top surface (few tens of nanometers of depth) of those films [16].

CONCLUSIONS

From XPS results that identified Tungsten doublets $W4f_{5/2}$ and $W4f_{7/2}$ in conjunction with the information obtained from ATR FT-MIR analysis about of the quasi-unaltered molecular structure of phosphotungstates ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) inside of PDMSUr-PWA samples constitute evidence of the presence of molecular and atomic Tungsten at top Surface (10 nm of depth) of these materials. Furthermore, considering the elastic (from PU and PDMS) and hardness (from ormosil and PWA) features that PDMSUr-PWA films exhibit, one can infer that these materials could constitute a structural support for PWA in applications of heterogeneous catalysis in chemical reactions e.g. hydrolysis and condensation under certain thermodynamic and kinetic conditions.

From characterization and analyses of these hybrid materials, it can be deduced that at PWA concentrations close to 35 w/w% of PWA (at which the W concentration is maxima), the Tungsten segregation at surface of these films is predominant, and also take in consideration the significant Bromine presence at surface at the concentration of PWA mentioned above, one could infer that this sample is candidate for application as anticorrosive coatings. Furthermore, taking advantage of the Proton conductivity of PWA this sample also could be considered as a mixed conductor (of protons and electrons),

which in the form of membranes fulfill the requirements in order to be used as fuel cells.

Nonetheless, more in-depth studies are necessary, in order to characterize the surface of PDMSUr-PWA films, and to determinate the species present (atomic, molecular, ionic) and their corresponding interactions, aiming the development of catalytic applications.

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