ISSN: 2687-8097
Scientific Journal of
Research and Reviews
DOI: 10.33552/SJRR.2022.03.000557
Iris Publishers

Mini Review



# PDMSUr-PWA Films: A Mini-Review

**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

**Received Date:** December 27, 2021

**Published Date:** January 28, 2022

## Abstract

Polyurethanes (PU) are widely used as high-performance adhesives, coatings, and elastomers. However, in order to overwhelm its limitation of high flammability constitutes the addition of Siloxane-based modifiers like Polydimethylsiloxane (PDMS). Nonetheless, PU/PDMS co-polymers present low hardness and tenacity. By this reason, these co-polymers are reinforced with silicate structures like ormosil (organically modified silicates), acting as a reinforcement agent. In turn, these ormosil can act as a suitable matrix to host polyoxometalates like phosphotungstic acid (H3PW12O40/PWA). Thus, in this sequence it is composed the PDMSUr-PWA films, which constitute new hybrid materials exhibit interesting mechanical and chemical (organic and inorganic) properties. These new films (object of this present Mini-review), exhibit the following features and potential applications:

a. Photochromic and photocatalytic properties, exhibiting balanced flexibility/stiffness features.

b. Potential candidates as Proton exchange membrane fuel cells (PEMFCs). The content of Bromine and the $H_2O_{(l)}$ present in these films can constitute a Hydrogen-Bromine ($H_2$-$Br_2$) fuel cell system, due to the action of the Phosphotungstates ($[PW_{12}O_{40}]^{3-}$) in the transport properties of these membranes.

c. Potential candidates as polymeric biomaterials, which would have many important uses in tissues reconstruction.

For the applications of these materials are necessary the correlation among structure, composition, and properties. Thus, it is expected that this review can collaborate in the development of these new materials, due to the variety of properties that they possess, being able to satisfy part of the demand of thermal and electrical insulators, as also the need of anticorrosive coatings that are specially required at the industrial sector.

**Keywords:** PDMSUr-PWA films, Synchrotron Radiation Micro-X-ray Fluorescence (SR-µXRF), Hybrid Materials, Bromine, Fuel Cells

## Introduction

Polyurethanes (PU) are widely used as high-performance adhesives, coatings, and elastomers due to their mechanical and chemical properties [1,2]. Polyurethane chemistry aims to the production technology of high-performance coatings, adhesives, and foams [3]. However, materials based on Polyurethanes (PU) present low fire-resistant. One option, in order to resolve this problem is the insertion of Polydimethylsiloxane (PDMS), which significantly reduce heat release. Among the properties of PDMS can be mentioned: low glass transition temperature ($T_g$), insulating properties, mechanical, thermal, and oxidative stabilities, and also biocompatibility [1,2]. Others benefits of using siloxanes is that these allow to the material that contain them to be more flexible and resistant to moisture, water, and aggressive media [4]. The presence of PDMS segments lends such characteristics to the material as thermal stability (caused by the introduction of Si–O bonds), low surface energy and water repellence, having potential use as biomedical devices (e.g. oxygenators) for microfluidics, soft-lithography, insulators, adhesives, protective coatings, etc. Polydimethylsiloxane (PDMS) is also used to produce micro/nano-devices based on a platform for cell culture [3,5]. Nonetheless, PU/PDMS co-polymers present low hardness and tenacity. PDMS presents some degree of incompatibility with the PU (segregation of phases), based on its low solubility and the nature of their corresponding interactions (chemical and physical). For this reason, in the PDMS/PU system are necessary, in order to form interlocking bonds and/or cross-linked structures, reinforcing agents that combining their properties. One example of this constitute ormosil structures (organically modified silicates). Ormosil reinforce these co-polymers through silicates structures, its achieved the compatibility among the organic phases present (from PU/PDMS and ormosil). Thus, the improvement of the mechanical and adhesion properties of these co-polymers can be obtained using an amino-functionalized alkoxysilane, as a capped and/or finisher-chain groups [1,2]. The sol–gel chemical route was chosen for the synthesis of hybrid ormosil based on a polydimethylsiloxane backbone linked by urethane bonds by means $CO_2$ cycloaddition chemical reaction as an intermediate step [6]. The Sol-Gel process generates regions of ormosil inside this hybrid material, which structure is based on the crosslinking that starts with the hydrolysis process, catalyzed by Phosphotungstic acid (PWA), followed by silanol condensation and ormosil formation (RO–Si–O–Si–R) [3]. Ormosil matrix can constitute host for polyoxometalates like phosphotungstic acid ($H_3PW_{12}O_{40}$/PWA) constituting in this mode PDMSUr-PWA films, which exhibit interesting photochromic, photocatalytic, and mechanical properties. These materials exhibit hydrophilic and hydrophobic domains, which would favor uses as membranes for fuel cells, photochromic applications (adhesives in laminated windows, smart windows) [7]. For example, the incorporation of phosphotungstic acid (PWA) produced a hard material (20–60 MPa), and the elastic modulus rose by more than a hundred times as the PWA content increased [3]. PDMSUr constitutes a hybrid adhesive and, when is functionalized with alkoxysilane groups can be bind onto the interfacial hydroxyl groups of hydroxide/ carbonate layer by means of the sol–gel reactions, meanwhile the silanol groups can bind through Si–O–metal links [8]. The final product consists of a hybrid urethanesil (PDMSUr) with PWA molecules incorporated into the matrix. These materials also have potential applications such as protective coatings against corrosion in basic, saline and acidic media, in which the PWA playing an important role in this characteristic [3]. In the biomedical field, the PDMSUr-PWA films are used in implants, catheters, heart valves, due to their biocompatibility, low toxicity, and thermal and chemical stability. These films were deposited, in order to form a coating against the corrosion (through of a hydrophobic physical barrier formed), on metallic surfaces as Ti6Al4V and SS316L in biomedical grades [8]. In case of corrosion, these metallic surfaces release toxic vanadium and/or nickel ions, which are not biocompatible with the human body, being able to generate cytotoxicity, inflammatory reactions and, genotoxicity. In order to deposit (bind) the PDMSUr-PWA films on Ti6Al4V and SS316L surfaces, these previously have to be treated (formation of rough oxides layers) by procedures based on low-pressure plasma activation and pulsed Nd: YAG laser. X-ray Photoelectron Spectroscopy (XPS) analysis revealed the formation of thin oxide reactive layers of $TiO_2$ and $Fe_2O_3$ on the surfaces of Ti6Al4V and SS316L respectively [8]. The efficacy of adhesion was estimated by performing Pull-off tests and by the comparison of treated and non-treated substrates by low pressure plasma and laser. These tests showed a significant increment in the adhesion (more than 100%) of PDMSUr coatings in comparison with the biomedical grade metals (stainless steel and titanium alloy) untreated [8]. The adhesion strengths of PDMSUr films on metallic and glass surfaces presented values up to 7 MPa at a maximum temperature of 160 °C [3]. The hybrid coatings have potential use for metallic surfaces employed as orthopedic and dental implants [8].

PDMSUr films can also constitute polymeric biomaterials have many important uses in tissue reconstruction. However, one of the biggest problems faced by these biomaterials is the infection by bacteria, which can be prevent by the use of surfaces that prevents bacterial adhesion (properties influenced by solvation forces, steric interactions, etc.) [9]. Specific and non-specific interactions (physical, chemical, and biological in origin) participate in cell fixation. Segmented polyurethanes have been used as biomaterials due to their biocompatibility, mechanical resistance, and flexibility. Silicones and polyurethanes have applicability in the biomedical area as aesthetic and reconstructive implants, used together or separately. PDMSUr films synthesized showed relevant cytocompatibility, which was observed by means of adhesion of fibroblast and osteoblast cells. This adhesion could be related with the hydrophilic characteristics (based on the polar groups e.g. hydroxyls and ether), at surface, according to X-ray photoelectron spectrometry (XPS). Furthermore, the films of PDMSUr presented good cytocompatibility and bacteriostatic behavior against the adhesion of Gram positive (*L.casei*) and Gram-negative (*E.coli*) bacteria, being that in this later the amount of PWA in the polymeric matrix had an influence on the adhesion of this bacterium to the films. Electrostatic and Van der Waals forces are among the interactions that influence this bacterial adhesion on PDMSUr surfaces [9]. Tests were performed in order to analyze the antimicrobial activity of these materials with three bacteria: *Escherichia coli, Staphylococcus aureus and Enterococcus faecium*. The results proved its efficiency eliminating from 95 to 100% of the pathogens [4].

PDMSUr films could be prepare without pores, exhibiting resistance to the decomposition through of the hydrolysis of urethane bonds. Other properties of these coatings including: wettability, hardness, and roughness, which play an important role in the adhesion of fabrics. Nonetheless, more studies are necessary in order to know the biocompatibility and cytotoxicity of these films, as also to discover the possible mechanisms of adhesion of bacteria on the substrates considered [9].

PDMSUr-PWA films also can be considered as potential candidates for Proton exchange membrane fuel cells (PEMFCs). As in these nanomaterials there is presence of Bromine, could be given the conditions for an improved $H_2$-$Br_2$ fuel cell and battery system. There is segregation of Bromine at surface and through of the thickness of PDMSUr-PWA films, which is function of PWA concentration mainly. The presence of Bromine in PDMSUr-PWA films can be correlated with their adhesive, thermal-insulation, and anti-corrosive properties. PDMSUr-PWA films can constitute systems for the storage/supply of energy at macro/micro/

molecular/atomic scales [10].

From characterization and analyses of these hybrid materials, it can be concluded that there is a predominant tungsten (under the form of phosphotungstates $[PW_{12}O_{40}]^{3-}$) segregation across the thickness of the films at PWA concentrations higher than 50 w/w%. At PWA concentrations less than 35 w/w%, the tungsten segregation at surface of these films is predominant, based probably on the electrostatic interactions among PWA with ormosil and amine groups. At PWA concentrations less than 15 w/w%, the electrostatic interactions between PWA and amine groups possibly predominate. The different properties (mechanical and chemical) that these films exhibit depend possibly to the inhomogeneity in PWA distribution patterns (demonstrated at micrometric and millimetric levels). Referent to these films were elaborated models of tungsten/phosphotungstates distribution in function of PWA concentrations, in order to correlate structure, composition and properties [7].

Recently, it has developed a method in order to fabricate a biocompatible PDMS surface (coated with an herbal extract), which exhibits antibacterial and anticancer characteristics [5]. PDMSUr-PWA films can be also adaptable to these characteristics, despite to the fact that native PDMS surface inhibits cell adhesion, due to the oligomers of urethanes allow this. Furthermore, under surface treatment PDMS domains in these films can also adhere bacteria and cells.

## Conclusion

From the investigations done about these hybrid materials (2011-2015) in the research group that I was pertaining, in conjunction with supporting additional investigations about materials based on Polyurethanes (PU)/Polydimethylsiloxane (PDMS) copolymers, this revision arises, in order to collaborate in the development of these new films, due to the varied properties that they possess, being able to satisfy part of the demand of thermal and electrical insulators, as also the need of anticorrosive coatings that are specially required at the industrial sector. PU/PDMS based co-polymers present as drawbacks low hardness and tenacity. By this reason, they are reinforced with silicate structure like ormosil (organically modified silicates), acting as a reinforcement agent. In turn, these ormosil can act as a suitable matrix to host polyoxometalates like phosphotungstic acid (H3PW12O40/PWA). Thus, in this sequence it is composed the PDMSUr-PWA films (containing PDMS, Urethanes, Polyurethanes, Silicates and PWA), which constitute new hybrid materials exhibit interesting mechanical and chemical (organic and inorganic) properties. These new films exhibit the following features and potential applications:

**I.** 1.Photochromic and photocatalytic properties, exhibiting balanced flexibility/stiffness features also.

**II.** 2.Potential candidates as Proton exchange membrane fuel cells (PEMFCs). The content of Bromine and the H2O(l) present in these films can constitute a Hydrogen-Bromine (H2-Br2) fuel cell systems, due to the action of the Phosphotungstates ([PW12O40]3–) in the transport properties of these membranes.

**III.** 3.These new hybrid materials can be used as coatings for corrosion protection in different media.

**IV.** 4.Potential candidates as polymeric biomaterials, which would have many important uses in tissues reconstruction.

Nonetheless, the applications of these materials require the more in-depth knowledge about correlation among structure, composition, and properties.

## Acknowledgments

The author thanks to the Sao Paulo Research Foundation (FAPESP) by the research grants (2011/08120-0, 2011/06019-0 and 2013/05279-3) and to the CNPq Brazilian agency by the financial support (research grants 141880/2011-2 and 160515/2011-4); to the Dr. Carlos Perez for his help at the XRF measurements done at Brazilian Synchrotron Light Source (LNLS); to the CNPEM-LNLS facilities for SR-GIXRF and SR-µXRF measurements (proposals number: XAFS1 14254 and XAFS1 14257 respectively). We also extend our gratitude to Dra. Marcia A. Rizzutto for the EDXRF measurements, with the Amptek portable spectrometer, at Institute of Physics of the University of Sao Paulo (IF-USP); to Dr. Vera Luzia Salvador, Dr. Ivone Sato and Dr. Marcos Scapin for the WDXRF measurements, with the Rigaku RIX3000 spectrometer, at the Laboratory of X-ray Fluorescence (XRF) of the Centro de Quimica e Meio Ambiente (CQMA) from Nuclear and Energetic Research Institute of Sao Paulo-SP-Brazil (IPEN/CNEN-SP); and to the Analytical Center of the Institute of Chemistry from the University of Sao Paulo (CA-IQ-USP). The authors also extend their gratitude to Prof. Dr. Francisco Krug and Dr. Lidiane C. Nunes of the Analytical Chemistry Laboratory of CENA-USP (''Henrique Bergamin Filho'') for the LIBS measurements, and Prof. Dra. Márcia A. Rizzutto for the EDXRF measurements performed at the Institute of Physics of the University of Sao Paulo (IF-USP). Finally, the author thanks to Dr. Michael Noeske from Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung (IFAM, Bremen-Germany), to Prof. Wagner Polito of the Institute of Chemistry of Sao Carlos, University of Sao Paulo, Sao Carlos-SP-Brazil (IQSC-USP) for his advice; and to the Inorganic Hybrid Materials Chemistry Group (GQMATHI-IQSC-USP) for the discussions and suggestions.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. L. Wang, Q. Ji, T. Glass, T. Ward, J. Mcgrath, et al. (2000) Synthesis and characterization of organosiloxane modified segmented polyether polyurethanes. Polymer 41: 5083-5093.

2. M. Pergal, J. Dzunuzovic, R. Poreba, D. Micic, P. Stefano, L. Pezo, M. Spirkova (2013) Surface and thermomechanical characterization of polyurethane networks based on poly(dimethylsiloxane) and hyperbranched polyester. Express Polymer Letters 7(10): 806-820.

3. K. M. F. Rossi de Aguiar, E. P. Ferreira Neto, S. Blunk, J. F. Schneider, et al. (2016) Hybrid Urethanesil Coatings for Inorganic Surfaces Produced by Isocyanate-Free and Sol-Gel Routes: Synthesis and Characterization. RSC Adv 6(23): 19160-19172.

4. (2021) Material feito com $CO_2$ é capaz de evitar infecções por fungos e bactérias. Instituto de Química de São Carlos. Assessoria de Comunicação do IQSC/USP.

5. Jiao, J (2016) Antibacterial and anticancer PDMS surface for mammalian cell growth using the Chinese herb extract paeonol (4-methoxy-2-hydroxyacetophenone). Sci. Rep. 6: 38973.

6. K. R. Aguiar, V. G. Santos, M. Eberlin, K. Rischka, et al. (2014) Efficient Greensynthesis of Bis (Cyclic Carbonate) Poly (Dimethylsiloxane) Derivative Using $CO_2$ Addition: A Novel Precursor for Synthesis of Urethanes. RSC Adv 4(46): 24334-24343.

7. O. Elguera, K. Rossi de Aguiar, C. Zamboni, W. Polito, U. P. Rodrigues-Filho (2020) "Qualitative and Semiquantitative Determination of the Atomic and Molecular Tungsten Distributions in Hybrid Hydroxyurethanes-Poly(dimethylsiloxane) Films Containing Phosphotungstates ($[PW_{12}O_{40}]^{3-}$)". Applied Spectroscopy. 74(12):1515-1529.

8. K. M. F. Rossi de Aguiar, U. Specht, J. Maass, D. Salz, C. Picon, (2016) Surface modification by physical treatments on biomedical grade metals to improve adhesion for bonding hybrid non-isocyanate urethanes. RSC Adv 6(53): 47203-47211.

9. K. Rossi Flores de Aguiar (2015) Síntese de Hidroxiuretana-Poli(dimetilsiloxano) com Diferentes Terminações de Cadeia via Fixação de $CO_2$: Síntese, Caracterizações e Aplicações. Instituto de Química de São Carlos. São Carlos, São Paulo-Brasil: Universidade de São Paulo (IQSC-USP).

10. Orlando Elguera Ysnaga (2020) Qualitative and Semiquantitative Determination of Bromine in Hybrid Hydroxyurethanes-Poly(dimethylsiloxane) Films Containing Phosphotungstates ($[PW_{12}O_{40}]^{3-}$)". Engineering Physics 4(2): 19-36.

**Citation**: Orlando Elguera Ysnaga. Pdmsur-PWA Films: A Mini-Review. Sci J Research & Rev. 3(3): 2021. SJRR.MS.ID.000557.
DOI: 10.33552/SJRR.2022.03.000557.