PDMS-urethanesil hybrid multifunctional materials: combining CO₂ use and sol–gel processing

Maria C Rocha, Michel Wong Chi Man, Maria Do Carmo, A J Mainardi,
Ubirajara Pereira Rodrigues-Filho, Florian Günther, Elton F S Lima, Kelen
M F Rossi de Aguiar, Jefferson R Bearzi, Mateus B Simões, et al.

► To cite this version:

Maria C Rocha, Michel Wong Chi Man, Maria Do Carmo, A J Mainardi, Ubirajara Pereira Rodrigues-Filho, et al.. PDMS-urethanesil hybrid multifunctional materials: combining CO₂ use and sol–gel processing. *Journal of Sol-Gel Science and Technology*, 2020, 95 (3), pp.693-709. 10.1007/s10971-020-05376-y . hal-03094364

HAL Id: hal-03094364

<https://hal.science/hal-03094364>

Submitted on 4 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

PDMS-Urethanesil Hybrid Multifunctional Materials: Combining CO₂ use and Sol-Gel Processing

Authors: Florian Günther^{1,2}, Elton F. S. Lima¹, Kelen M. F. Rossi de Aguiar³, Jefferson R. Bearzi³, Mateus B. Simões¹, Ricardo Schneider³, Rafael A. Bini³, Sidney J.L. Ribeiro⁴, Michel Wong Chi Man⁵, Klaus Rischka⁶, Flávio H.B. Aguiar⁷, Renata Pereira^{6,7}, Maria do Carmo A. J. Mainardi^{6,8}, Marina C. Rocha⁹, Iran Malavazi⁹, Tânia A. Pasetti¹⁰, Marcio L. Santos¹⁰, Hidetake Imasato¹, Ubirajara Pereira Rodrigues-Filho^{1*}

Affiliation:

¹ Grupo de Química de Materiais Híbridos e Inorgânicos (GQMATHI), Instituto de Química de São Carlos, Universidade de São Paulo (USP), São Carlos, Brazil

² Grupo de Polímeros, Instituto de Física de São Carlos, Universidade de São Paulo (USP), São Carlos, Brazil

³ Group of Polymers and Nanostructures (GPAN), Federal University of Technology – Paraná (UTFPR), Toledo, Brazil

⁴ Institute of Chemistry, Universidade Estadual Paulista (UNESP), Araraquara-SP, Brazil

⁵ Institut Charles Gerhardt Montpellier (ICGM), University of Montpellier, CNRS, ENSCM, Montpellier, France

⁶ Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Bremen, Germany

⁷ Department of Restorative Dentistry, Piracicaba Dental School, Universidade de Campinas (UNICAMP), Piracicaba, São Paulo, Brazil

⁸ Faculdade de Odontologia do Centro Universitário Hermínio Ometto – FHO – Uniararas

⁹ Departamento de Genética e Evolução, Centro de Ciências Biológicas e da Saúde, Universidade Federal de São Carlos (UFSCAR), São Carlos, Brazil

¹⁰ Biotechnology and Innovation in Health and Pharmacy Graduate Program, University Anhanguera at São Paulo (UNIAN-SP), São Paulo, Brazil

**Corresponding author: ubirajara@usp.br*

If available, the 16-digit ORCID of the author(s)

Florian Günther 0000-0001-5002-4172

Kelen M. F. Rossi de Aguiar 0000-0002-4285-4050

Jefferson R. Bearzi 0000-0003-3277-7984

Mateus B. Simões 0000-0001-7778-8914

Elton F. S. Lima

Flávio H.B. Aguiar 0000-0003-3389-5536

Renata Pereira 0000-0002-7865-3365

Maria do Carmo A. J. Mainardi 0000-0001-7288-5424

Ricardo Schneider 0000-0001-9501-8489

Rafael A. Bini 0000-0001-9036-3654

Sidney J.L. Ribeiro 0000-0002-8162-6747

Michel Wong Chi Man 0000-0003-1390-4239

Klaus Rischka 0000-0003-3427-4037

Hidetake Imasato

Ubirajara Pereira Rodrigues-Filho 0000-0001-6913-8540

Iran Malavazi 0000-0002-4526-4961

Marina C. Rocha
Márcio L Santos 0000-0002-6607-1640
Tânia A Passeti 0000-00028541-0986

Abstract

CO₂ mitigation by cycloaddition to bis-epoxides to obtain bis-cyclocarbonates (CC) paved one way to a new class of polyurethanes (PUs), the non-isocyanate polyurethanes (NIPUs). By using molecules functionalized with alkoxysilyl groups as end chain it is possible to obtain hybrid NIPUs, also called urethanesils, by Sol-Gel chemistry. Using bis-cyclocarbonate polydimethylsiloxane (CCPDMS) with proper diamines and end-chain amino silanes followed by sol-gel processing leads to versatile hybrid non-isocyanate polydimethylsiloxane urethanes (PDMS-urethanesil). This review reports—besides our recent studies about PDMS-urethanesil materials—the sol-gel chemistry applied to synthesize urethanesil and its applications. While the antimicrobial, photochromic, and anticorrosion properties of urethanesil loaded with phosphotungstic acid as well as the luminescent effect of material loaded with Eu³⁺ have already been reported, antimicrobial features of urethanesil loaded with phosphoric acid are our newest findings which we herein report for the first time. The impact of the inorganic acid used on the sol-gel process is highlighted together with the importance of antibiofouling properties. Although the antibiofouling mechanism is still under investigation, the broad spectrum of action of phosphoric acid loaded urethanesil is worth mentioning, since it has been tested to be efficient against some pathogenic bacteria including a drug resistant *Staphylococcus aureus* strain as well as pathogenic fungi and yeast. Due to the simple, straightforward, and highly reproducible synthesis as well as the opportunity to obtain versatile materials with tuneable mechanical and physical properties, this new class of hybrid materials promises to be applicable in different industrial fields.

Keywords

Non-isocyanate polyurethanes, inorganic-organic hybrid, polydimethylsiloxane, biomedical coatings, photonic, anticorrosion

Graphical abstract

Highlights

- Combining CO₂ use and Sol-Gel processing yields versatile PDMS-Urethanesils with tunable properties
- Key approach: combine non-isocyanate PU with silica and PDMS through aminolysis of cyclocarbonate
- Morphology control using inorganic acid as catalyst for sol-gel process
- Inorganic loading defines the application, e.g. as anti-corrosion coating or as white light emitter
- Novel finding with new applications, e.g. antimicrobial activity against pathogenic microorganisms

1. Introduction

Polyurethanes (PUs) are considered as a special group of polymeric materials having many different applications and are present in our everyday life, for instance as material in furniture, cars, clothing, shoes, elastomers, coatings, wall and roofing insulation, and many others [1–4]. Two main aspects drive the development of novel PU materials. First, new types of functionalities are desired to improve the performance of PUs in their existing fields of application or to open up new uses. Second, novel synthetic strategies are of interest to the PU industry in order to enhance sustainability. For example, combining PUs and silica leads to hybrid materials with high performance, so-called urethanesils [5]. This second aspect is also particularly important, since the conventional fabrication routes require the use of isocyanate functional groups. The international community, however, has emerged with concerns about the toxic effects of isocyanate exposure to humans. These include skin irritations, chest tightness, and difficulty in breathing, besides being a potential human carcinogenic compound [6]. To avoid the impact of isocyanates in the synthesis of PUs, research on non-isocyanate polyurethanes (NIPUs) are of great interest for both academic and industrial sectors [7–10].

Among many approaches, the aminolysis of cyclocarbonates (CCs) is one of the most practical strategies for three main reasons in addition to the isocyanate-free aspect: firstly, it allows synthesizing NIPUs at mild reaction conditions without the emergence of by-products, secondly, the CC precursor can be obtained via insertion of Carbon dioxide (CO_2) to epoxides, and finally, hydroxyl groups next to the urethane bond are formed. The latter two aspects are particularly important. On the one hand, it is essential to use CO_2 as raw material to produce valuable and market-competing products to reduce the total emission to the atmosphere and to face global warming [11–13]. On the other hand, the additional hydroxyl groups of hydroxyurethanes (NIPUs) have a great impact on microphase separation through intra- and intermolecular hydrogen bonding to nitrogen or oxygen atoms on different segments [14–16]. Also, it provides better hydrolysis resistance being moisture insensitive [7] compared to conventional polyurethane system. Thus, simple NIPU polymers have inferior mechanical and physical characteristics in comparison to conventional PUs. This raised interests in developing hybrid compositions of NIPUs by subsequent cross-linking with chain extenders or poly-functional reactants such as aminosilanes, polyamines, and polycyclocarbonates [17–19]. One of such compounds is poly(dimethylsiloxane) (PDMS), which is

classified as a silicone and can be used to build different types of devices including implants, microfluidic devices, microchips, water repellents, membrane for gas permeability, lithography, antifouling coating for marine environment and many others [20–23]. Over the past years, our research network worked on the synthesis of hybrid NIPUs from PDMS-based bis(cyclocarbonate) with (3-aminopropyl)triethoxysilane (APTES) as chain coupling agent [24] leading to the formation of different materials with potential applications as protective and antimicrobial coatings [25] or photonics [26].

In this article, some important research studies related to PUs and NIPUs are explored. It is structured as follows. In section 2, the synthetic strategies are summarized: first the conventional approach to form PU, second the sol-gel process to obtain urethanesils, and third the aminolysis of CC to form NIPUs. A stronger focus is given to the last point consisting of the CO₂ fixation to epoxy groups and the aminolysis of CC as they are essential key reactions for our studies. Subsequently, section 3 is focussed on PDMS- and silica-based NIPUs; particularly those derived from APTES, are gathered up and the impact of inorganic acids as catalyst in the sol-gel process on the morphology of the obtained material is considered.

Figure 1 Molecular structure of a thermoplastic polyurethane elastomer.

In section 4, potential applications of PDMS-based urethanesils are detailed reviewed covering the areas of protective coatings, photonics, and antibacterial membranes. The first two of these applications have been reported in literature over the last years and were based on pristine, phosphotungstic acid (HPW) loaded [27–30], or Eu³⁺ loaded urethanesils [26]. Aiming at enlarging the area of applications of PDMS-based NIPUs, new, phosphoric acid loaded materials are currently of our interest [31]. For those, we found antibacterial and antifungal activities, which are communicated here for the first time.

2. Synthesis of Polyurethanes

2.1 Traditional Route

The conventional route to synthesize PU materials goes back to 1937, when the German Chemist Otto Bayer and his co-workers established the production of PU by polyaddition of diisocyanate and polyol [3, 32]. As depicted in Figure 1, most PU materials consist of two building blocks: a rigid and a soft segment, which are linked via a urethane bond. Up to now, most PUs

are synthesized in the same way following a two-step methodology. The first step corresponds to a reaction between a polyol and an excess of diisocyanate to obtain a pre-polymer. The second step consists in the reaction of this pre-polymer with another polyol as chain extender or crosslinking agent [33]. Many biomedical applications [33, 34] such as spinal devices [35], scaffold for tissue regeneration [36], osteochondral implant [37], breast reconstruction [38], and so on, have been documented based on the fine tuning of the soft and hard segments. Moreover, the progress in processes, additives, and techniques has allowed infinity of formulations that contributed to increase the number of applications for PU

materials that continue instigating the growing global market [39]. Isocyanate precursors, however, are very harmful at each stage of the life cycle of the polyurethane. Sustainable routes to obtain PUs can circumvent environmental and human health drawbacks of this material which can negatively impact their future applications [40, 41].

2.2 Sol-gel chemistry towards hybrid PUs

While most of the traditional PUs belong to the class of organic materials, in the past years there has been a growing interest in PU materials containing silica or silicone additives or both [42, 43]. Compared to polymers with carbon backbones, the presence of siloxane results in increased

Figure 2 The scheme of aliphatic polyurethane-silica composite preparation using pre-polymerization technique. Figure taken from [52].

thermal stability, higher mechanical strength, and chemical resistance [34, 35]. This high stability is mainly due to high Si-O bond dissociation energy [44] the reason of which as well as of the unusual large bond angles was recently assigned to hyper-conjugative interactions of $LP(O) \rightarrow \sigma^*(Si-R)$ type [45, 46] although this issue is debatable [47].

The combination of organic and inorganic materials entangled on a molecular level yields products which are typically referred to as hybrid materials [48]. This term, however, is used for many different systems comprising a wide range of materials, such as crystalline highly ordered coordination polymers, amorphous sol-gel compounds, or materials with chemical and physical interactions between the inorganic and organic units. All these materials are typically synthesised via sol-gel processes, with or without hydrothermal conditions. Such a process is frequently used to prepare polymer composites containing silica in order to improve thermal stability, scratch resistance, tensile strength, and transparency [49–51]. For example, Pavličević synthesised novel aliphatic polyurethane-silica hybrid films using a pre-polymerization method in the presence of spherical, submicron amorphous SiO_2 [52]. It was found that low amounts of silica act as a dispersing agent between soft and hard segments and cause a remarkably improved thermal

stability and mechanical properties for the obtained PU composites (Figure 2). In another study, He *et al.* investigated the effect of a mixed sol-gel precursor on the viscoelasticity as well as on the mechanical and the coating properties of a series of inorganic-organic hybrid urethane coatings [53]. Considering mixed sol-gel precursors—in particular mixtures of Tetraethylorthosilicate, Titanium(IV) isopropoxide, and Zirconium(IV) propoxide in different molar ratios—as the inorganic phase and cyclohexane-based polyester polyol reacted with hexamethylene diisocyanate isocyanurate (3HDI), hetero-bonded silicon-oxygen-metal colloids were formed. It was discovered that the mixed sol-gel precursor with equal weight percentage ratio of the three materials resulted in an increase of the glass transition temperature compared to other ratios. The authors related this observation to a decreased size of the inorganic phase and consequently an increase of the interface between the inorganic and organic phases.

Another example of how the introduction of silica in PU materials enhances the mechanical properties was published by Bonab and co-workers who prepared hybrid inorganic-organic nanocomposite foams of silica aerogel and PU for thermal insulation [54]. They reported that with the increase in nanoparticle content, the cell size distribution was broadened and the cell density was decreased. According to

their results, the addition of 0.5 up to 1 wt% of silica aerogel enhances the mechanical properties of the PU nanocomposite foams.

The higher demand for waterborne coatings propels the production of water-soluble PUs. These waterborne finishes have a broad variety of applications; including automobiles, concretes, furniture, plastics, woods, and even printing inks. They are also compatible with both conventional and electrostatic application equipment. Commercial waterborne PUs, such as Baymedix® FD and CD, are medical-grade PUs used to manufacture absorbent, breathable, skin-friendly adhesives for backing films and surgical gloves.

Besides PU, polyacrylate (PA) is another ubiquitous polymeric binder used in waterborne coating systems. While PA exhibits water and chemical resistance, weathering properties and hardness, and low cost production [55], PU shows elasticity, scratch resistance, flexibility and toughness [56]. Hence, the two materials look promising for improved waterborne coatings on combining those advantages. For instance, aiming to combine both polymer technologies with polysiloxane, Chinese researchers synthesized polysiloxane urethane acrylate (PSi-IPDI-HEA) by reacting polysiloxane (PSi), isophorone diisocyanate (IPDI) and 2-hydroxyethylacrylate (HEA) with and without long chain modifiers [57]. It was

found that the system of PSi-IPDI-HEA has excellent yellowing resistance, which is caused by photo-oxidation or photo-degradation of polymers and coatings upon UV irradiation.

In another work, Cakić *et al.* successfully prepared a series of waterborne PU adhesives through a sol-gel process using different amounts of isophorone diisocyanate as hard segment, recycled castor oil-based polyols as soft segments, and APTES as chain organosilica former as well as covalent coupling reagent. The amino group of APTES reacts with isocyanate forming the interfacial bond between the silica and the PU. The authors concluded that the glass transition temperature and particle size of PU nanocomposites were dependent on silicate concentration, which is based on the alkoxysilane content. The experimental results revealed that APTES and the hard segment contents play a key role in controlling the structure and the properties of the PU cast films based on castor oil-recycled polyols [58].

2.3 Non-isocyanate polyurethanes

Over the past years, different processes for producing non-isocyanate polyurethane (NIPU) have been investigated which can majorly be grouped into four approaches [2] where the polyaddition is the most attractive method from an environmental- and health-friendly point of view [59–64]. In this approach, cyclocarbonates react

Since the first report of the aminolysis of CC, the procedure has been applied in various ways, such as using compounds with two or more cyclocarbonates, which yields NIPUs in a single reaction step (Figure 3 b). In this case, additional hydroxyl groups are present next to the

[illegible]

9

compared to virgin epoxy samples, which was assigned to a decrease in the crosslink density. More importantly, the glass transition temperature was shifted to higher values which is likely due to hydrogen bonding limiting the segmental motion of the polymer chains. The possibility to form hydrogen bonding plays furthermore an important role in case of NIPUs obtained by co-polymerization of cyclic and aromatic cyclic carbonates, for instance diglycidyl ether bisphenol A or Araldite CY230, with poly(propylene glycol) bis (2-amino propyl ether) [71]. Here, self-assembling among the chains triggered by H-bonding leads to folded-sheet morphology and thermoreversible adhesion.

Cyclocarbonates are the primary reactants in the synthesis of the non-isocyanate polyhydroxyurethane. The synthesis of this precursor compound reveals another environment-friendly argument for the cyclocarbonate polyaddition route to fabricate PUs. Starting from corresponding epoxy precursors, cyclocarbonates can be obtained by chemical fixation of CO₂, which is not only non-toxic but also easily renewable as well as abundantly available and, therefore, inexpensive. Moreover, making use of stored CO₂ to produce valuable products helps in achieving negative emission technologies. Over the last years, several reviews on the synthesis and the catalytic preparation of cyclocarbonates from epoxides and CO₂

were published [2, 72, 73]. As highlighted by North *et al.*, the production of cyclocarbonates requires highly purified CO₂ as well as high temperatures and pressures. Bimetallic aluminium (salen) complexes used as catalyst, however, has the potential to allow this process to be performed at or near room temperature and pressure [72].

In summary, the ever-growing literature illustrates the wide range of properties achieved by these eco-friendly PUs. In the next section, we will address the class of PDMS-based NIPUs and their combination to silicates, i.e. PDMS-urethanesil, as well as their properties.

3. Non-isocyanate PDMS-Urethanesils

3.1 PDMS based NIPU materials

The consideration of the ring-opening polymerization as reviewed in section 2.3, was only based on the key compounds needed to perform the reaction: the amine and the cyclocarbonate. The general concept, however, opens a large playground to tailor the material by choosing a suitable reactant structure. As described in section 2.2, the introduction of silicone- and silica-based substructures enhances the mechanical, chemical, and physical properties of PU materials. Polydimethylsiloxane (PDMS) can be used for this purpose. The backbone of PDMS features alternating Si and O atoms and

two methyl groups on each silicon atom. This chemical structure gives rise to an enormous number of applications [22, 74, 75], which is mainly for the following three characteristics: a) the energy barrier for rotation of the chain around the siloxane backbone is very small which renders the polymer very flexible, b) the compact methyl groups are highly non-polar which leads to intermolecular, fluctuating dipole-induced dipole interaction, i.e. London dispersion force, and c) the large Si-O-Si bond angles which result in low hydrogen-bonding interaction energies of maximal $11.05 \text{ kJ mol}^{-1}$ for an angle of 105° in a siloxane–water complex [45]. The combination of these features is essential for the rubber-like elasticity and the uniquely high flexibility of PDMS materials and the low Hansen polar and H-bonding solvency parameter, hydrophobicity and low liquid water permeability [76–78].

Because of its properties, PDMS is an interesting soft component to tailor the properties of PU materials. For instance the wettability can be reduced, the surface energy can be decreased, the glass transition temperature and the melting point can be lowered, the cell-adhesive property can be improved, or the bendability and even stretchability can be tuned. In order to synthesise PDMS-urethane (PDMSUr) materials using the aminolysis of cyclocarbonates, our research network reported on the preparation of PDMS with terminal cyclocarbonate groups (CCPDMS) utilizing the cycloaddition of CO_2 to epoxy rings [24]. For this precursor, the reactivity with amines was tested in the past years. In particular, 3-Aminomethyl-3,5,5-trimethylcyclohexylamine (isophorone diamine, IPDA) and phenylethylamine (PEA) were considered as chain extensor

Figure 4 Diamines and amines considered as chain extensors and chain terminator, respectively.

and chain terminator groups, respectively, and a high conversion of CCPDMS to PDMSUr was found. In a more recent work [69], we tested further diamine compounds as novel potential chain extensors including aromatic and aliphatic amines (Figure 4). We observed that aromatic amines do not react in our experimental conditions, which is due to the positive mesomeric effect of the amine attached to an aromatic system. In opposition, all tested aliphatic amines showed a high conversion towards PDMSUr. Furthermore, we recently reported dopamine as promising chain terminator group [30], which distinguishes itself from PEA via the catechol group. This functionalization allows a chemical bonding to metal-oxide layers yielding high resistance against mechanical and chemical forces due to covalent metal-oxide interfacial bond [79–81].

Besides our work, other groups use similar approaches to synthesize novel PU materials and look for potential applications. For instance, a series of novel cyclocarbonate-functionalized PDMS compounds were successfully developed by Liu *et al.* In their work, materials with different carbonate content were reacted with various diamines such as IPDA, 4,4'-diaminodicyclohexylmethane, 1,2-diaminopropane and 1,6-diaminohexane to form NIPU coatings [82]. Thermal and mechanical properties were evaluated and the results showed that cycloaliphatic

amine-cured coatings have higher tensile strength compared to the aliphatic amine-cured coatings. Furthermore, with the increase of the carbonate content, the tensile strength, Young's modulus and glass transition temperature of the coatings have been increased.

3.2 PDMS-Urethanesils

Nanocomposite silica- and silicone-based materials produced by using organo-alkoxysilanes leads to so-called Organic Modified Silicates (ORMOSILs) which can be considered as a sub-group of hybrid materials [5, 83–87]. PDMS-Ormosils are especially of interest due to the possibility to tune the mechanical features [88], the optical [89] properties, and the surface energy, the permeability, as well as the biocompatibility and the bioactivity [90]. PDMS-Ormosils have found applications in biosensors or as matrix materials for functionalized coating such as UV-protection, Ion-exchange, or metal corrosion protection. For example, Doro *et al.* [91] studied coatings made by the reaction of ormosils prepared from tetraethoxysilane (TEOS) and PDMS. The obtained coatings showed microphase separation and low surface energy due to the hydrophobic feature of the organosilane chemical structure. Furthermore, no alteration of cellular viability has been noted upon exposure to cytotoxicity assays. Additionally, no biofunctional change was observed throughout the migration assays for cells

with the PDMS and TEOS coatings. Therefore, it was concluded that these coatings were suitable for biomaterials in cardiovascular environment and other potential health applications such as incorporating bioactive species in order to prepare drug-eluting stents.

Using reactive aminoalkoxysilanes, the aminolysis reaction can be used to combine PUs with silica and form so-called urethanesils [92]. In doing so, improved mechanical and thermal properties can be induced to NIPU materials. Aminoalkoxysilanes, like APTES can concomitantly tune the urethane chain length and create covalently bonded organosilica domains within the material. The polysilsesquioxane network is formed alongside solvent evaporation as a result of the polycondensation reactions involving the silanol groups which results in an improvement of the properties of the pure PU [93]. A vivid proof of the organosilicate network is the T peak found at around -68ppm in the solid state Magic Angle Spinning (MAS) ^{29}Si Nuclear Magnetic Resonance (NMR) spectroscopy as exemplified for the PDMSUr1 and PDMSUr2 materials in Figure 5. The specific material compositions are given in Table 1. This T-peak refers to $\text{R-Si}(\text{OSi})_3$ bonds formed during the hydrolysis of APTES whereas the M- and D-peaks at 7.7 ppm and -22.3 ppm belong to $\text{R}_3\text{-Si}(\text{OSi})$ and $\text{R}_2\text{-Si}(\text{OSi})_2$ substructures, respectively, that majorly arise from the PDMS chain.

An approach towards similar materials as our PDMSUr was carried out and reported by Wu *et al.* who synthesized a hybrid waterborne PDMS silica hybrid via a two-step approach [94]. First, an amino-PDMS emulsion (DN 100) was prepared by aqueous sol-gel reaction of diethoxydimethylsilane (DEDMS) and APTES. Then, a Janus PU pre-polymer was prepared by reaction of Dibutyltin dilaurate (DBTDL), polypropylene glycol, 2, 2-Dimethylol propionic acid (DMPA), and

Figure 5 ^{29}Si MAS NMR of the PDMSUr1 and PDMSUr2 materials. The peaks which correspond to structures M, D and T structures are observed at their typical chemical shifts. Redrawn from Ref. [29]

1, 4-butanediol (BDO), and APTES. These polymers have one isocyanate as termination group opposed to a triethoxysilyl moiety. This triethoxysilyl end was obtained in similar fashion as our PDMSUr, i.e. using APTES amino groups to form a urethane bond. These alkoxy terminal groups underwent a sol-gel hydrolysis and condensation of Si-OH group of the DN 100, and established a siliceous network between PDMS segment and waterborne polyurethane chain [94]. In contrast to our approach, this strategy to synthesize the urethane moiety is still based on isocyanate compounds. Therefore, the obtained material does not belong to the class of NIPU. Nevertheless, this work is worth mentioning at this point,

since APTES is used as a coupling agent and silicate forming compound in a similar fashion as in our studies. In this way, the findings of Wu *et al.* pave the way to use the NIPU approach to produce new waterborne polyurethane-polydimethylsiloxane hybrid silica by replacing the isocyanates by the cyclocarbonates.

3.3 Inorganic Acids as sol-gel Catalyst and PDMSUr additive

Among the different combinations of chain extensors and chain terminators, IPDA and APTES (Figure 4) yield, so far, the best performing PDMSUr materials and have therefore been investigated more deeply in the past years. In particular, the hydrolysis rate of APTES towards

Table 1 Molar ratios of the precursors used to obtain the PDMSUr materials with different amount of inorganic acid.

Name	CCPDMS 1182 g/mol	APTES 221 g/mol	IPDA 170 g/mol	inorganic acid			Refs.
				type	wt%	amount	
PDMSUr1	1 mmol	3 mmol	-	-	-	-	[29]
				HPW	1	> 0.01 mmol	[27, 28]
				HPW	35	0.22 mmol	[27–29]
				HPW	55	0.35 mmol	[29]
PDMSUr2	1 mmol	2.25 mmol	0.75 mmol	-	-	-	[29]
				HPW	1	> 0.01 mmol	[27, 28]
				HPW	35	0.22 mmol	[27–29]
PDMSUr3	1 mmol	0.5 mmol	0.75 mmol	-	-	-	-
				H ₃ PO ₄	1	0.14 mmol	-

urethanesil, which can be boosted by adding an inorganic acid such as phosphotungstic acid (HPW) [29] or H_3PO_4 [31], was considered more deeply. Besides the catalytic effect, the acid contributes to further tunable properties of the material, which leads to potential applications, as it will be discussed in Section 4.

In our studies, on the one hand, the ratio of the precursors CCPDMS, APTES, and IPDA was varied. On the other hand, different percentages of acidic additives were considered [25, 27, 28, 31, 95]. The different compositions, which are presented in more detail here, are given in Table 1. The use of HPW as hydrolysis and condensation catalyst results in self-adhesive, corrosion-resistant and reversible photochromic hybrid coatings. In the material compositions, which we studied so far, the mass percentage of the HPW in the dry solid ranges from 0 to 55wt%. The sample with 35 wt% of HPW resulted in self-supported highly transparent yellowish films (Figure 6, on the right) [24].

Figure 6 Representative photograph of PDMSUR3:H₃PO₄ (1 wt%) (left) and PDMSUr1:HPW (35 wt%) (right) samples.

Recently, we prepared similar hydroxyurethanes as before testing different ratios of CCPDMS, IPDA, and APTES, but substituting H_3PO_4 for HPW [31]. The use of phosphoric acid, however, markedly affected the mechanical properties as well as the physical appearance. While compositions with larger amounts of IPDA resulted in sticky gels or sticky and elastomeric films, equal or smaller ratios with respect to CCPDMS yielded brittle up to self-sustained, resilient rubbers (Figure 7). A photographic comparison between the HPW loaded and the H_3PO_4 loaded materials is depicted in Figure 6. So far, no explanation is given

Figure 7 Images of the different phosphoric acid hydroxyurethanes obtained using different CCPDMS/APTES/IPDA molar ratios. The molar ratio for each material is shown in the lower side of each image.

Figure 8 SEM images of the cross-section of the acid free (a) and phosphoric acid loaded (b) PDMSUr3 materials in comparison to the 35wt% (c) and 55 w% HPW loaded (d) PDMSUr1. Subfigures c) and d) were reproduced from [29] by permission of The Royal Society of Chemistry[95].

why H_3PO_4 results in this different appearance when it was used in the urethanesil synthesis.

In order to characterize the morphology of the acid-free and the acid-loaded PDMSUr materials, Scanning Electron Microscopy (SEM) measurements were carried out for the cross-sections of PDMSUr1 containing 35wt% and 55wt% of HPW and the acid-free as well as the H_3PO_4 loaded PDMSUr3 materials. The obtained images are displayed in Figure 8. Whereas the acid-free and the acid-loaded PDMSUr3 materials show a predominantly homogeneous morphology, the

Table 2 EDS semi-quantitative analysis for agglomerates found in PDMSUr1:HPW (55wt%). The presented areas refer to the marked regions in Figure 8d).

Element	area 1		area 2	
	wt%	at%	wt%	at%
O	23.2	72.1	28.4	66.4
Si	3.5	6.2	15.9	21.1
W	71.9	19.4	54.5	11.1
P	1.4	2.3	1.2	1.4

PDMSUr1:HPW samples exhibit agglomerates displaying a wrinkled inner morphology [95]. Note, that due to the higher molar mass of HPW, which is of about 29 times larger than that of H_3PO_4 , the molar amount of added acid only differs by a factor of 1.5 when comparing PDMSUr1:HPW (35 wt%) to PDMSUr3: H_3PO_4 (1 wt%). It is unlikely that such difference in molar concentration would be responsible for phase segregation in these materials. A microanalysis of the regions, which are highlighted in Figure 8d, by means of X-ray emission energy dispersive spectroscopy (EDS) revealed a higher percentage of HPW in these agglomerates (Table 2). Furthermore, infrared and Raman spectroscopy measurements of these PDMSUr1:HPW materials have been performed but are not shown here. No sign of partial or total phosphotungstate decompositions were found. Hence, the agglomerates can undoubtedly be assigned to phosphotungstate-rich regions. Likewise, the differences in

appearance and, even more, in morphology between the phosphotungstic acid and phosphoric acid urethanesils lack of explanation. Possible reasons might be differences in solubility, hydrogen bonding, electrostatic interaction [96, 97], ion-pairing [98], or kosmotropic or chaotropic capacities [99–101].

4. Application

So far, we reviewed the strategies to synthesize PU and NIPU materials in general, as well as in combination with silicas to form urethanesils from sol-gel approach. Moreover, we showed exemplarily how inorganic acids yield different structural features of the obtained materials. In the following, we now focus on some already published and some recently obtained data, which indicate these PDMS-Urethanesils as promising candidates for future applications, especially for biomedical technologies.

4.1. Anticorrosive coatings

Applying special coatings opens the possibility to functionalize materials in order to improve or modify the surface properties. Such coating can either protect the material against the environmental conditions in which they have to operate, or they can introduce new functionalities to the material, which may enable new applications. Among others, metal surfaces are of particular importance, due to their widespread use in constructions,

transportation and logistics, vehicles, food industry, etc. While in transportation and logistics, special challenges are related to marine environment, chemical industry processing, such as biodiesel production for example [102], is performed using homogenous basic or acid catalysis [103, 104].

Metal alloy corrosion is even more relevant for biomedical applications. For instance, not only copper, nickel and magnesium suffer from corrosion when constantly exposed to biological fluids, but also stainless steel and titanium alloys. As a consequence, ion release is promoted to biological fluids [105–107]. To overcome this challenge, relevant coatings can isolate the underlying metal from the corrosive media and hence lower oxidation and associated device failures.

PU materials are often used as protective coatings not only due to their outstanding shelf-life, their fast application abilities, their strong adhesion, and their nearly unlimited film building properties, but also particularly because of their resistance against chemical environments, abrasion, and corrosion [108, 109]. However, some caveats still remain to be overcome such as the UV resistance under wet environment or saline conditions for PU coatings [110]. Recently, our group proposed hybrid polymeric coatings made of non-isocyanate PDMSUr as a novel and promising alternative [29]. In our studies, PDMSUr materials, which were

synthesized from CCPDMS and different proportions of IPDA and APTES, were investigated as implant coatings for the titanium alloy Ti6Al4V as well as the stainless steel SS307, an austenitic chromium-nickel stainless class. In addition to the pristine PDMSUr materials, coatings were tested to which HPW was added in different amounts. Due to its high acidity [111], HPW promotes the sol-gel process

of hydrolysis and condensation of APTES, thus producing a stronger solid PDMSUr.

The adhesion [29] properties of the obtained materials were investigated following three approaches to prepare the metal alloy surfaces before deposition of the polymeric films: no treatment, Nd:YAG pulsed laser treatment, oxygen plasma treatment [28]. In doing so, it was found that both physical treatments contributed

Figure 9 Polarization curve for bare Ti6Al4V, coated with PDMSUr1:HPW (35wt%) and PDMSUr2:HPW(35wt%) in Hanks physiological solution [28][28] (a) and for bare stainless steel SS307, coated with acid free and HPW loaded PDMSUr1 in seawater, basic, and acid media [29]. All potentials (V) are referenced to saturated calomel electrode. Reproduced by permission of The Royal Society of Chemistry.

to the formation of a thin layer of oxides (TiO_2 or Fe_2O_3) on the surface of the alloys, which improved the adhesion strength of PDMSUr by more than 100%. Moreover, the behaviour of the PDMSUr films containing 35 wt% of HPW was tested via corrosion essays. Specifically, the Ti6Al4V alloy samples without coating or coated with PDMSUr1:HPW (35 wt%) and PDMSUr2:HPW (35 wt%) were tested in Hank's solution. Figure 9a shows, that although the corrosion potentials of the coated samples are similar, as compared to the uncoated substrate, the current densities are tremendously reduced. More specifically, for the uncoated sample $1.68 \mu\text{Acm}^{-2}$ were measured, while 22.9 nAcm^{-2} and $0.295 \mu\text{Acm}^{-2}$ were obtained for the samples coated with PDMSUr1:HWP (35wt%) and PDMSUr2:HWP (35wt%), respectively [28]. Due to the different area of usage, the anticorrosion properties of the SS307 samples were tested in different media: seawater as well as in basic and acid media. As depicted in Figure 9b-d), the acid loaded coating shifted the corrosion potential significantly and lowered the current density by up to two orders of magnitude [29]. Although the acid-free coating yielded similar corrosion potentials as the uncoated SS307 sample, the current density was reduced by about a factor of 10. One possible explanation for this observation is that the polymeric layer suppresses the diffusion of charged species such as protons, dissolved oxygen and

even water from medium to metallic surface. Altogether, it can be concluded that the anticorrosion protection is not only due to the urethanesil coating, but there is a synergistic effect between the HPW and the PDMSUr material.

4.2 Antibacterial membranes and coatings

Chronic wounds associated with persistent pathologies or medical comorbidities can take up to 8 months to fully healing. Thus, antimicrobial dressings are necessary for efficient wound care. Hydroxyurethanes can be used as dressings, making the study of antimicrobial activity of the urethanesil hybrids an important issue for this type of application [112]. Hence, the PDMSUr materials obtained under the addition of HPW and H_3PO_4 were tested for antibacterial properties.

We studied the bacterial adhesion of the gram positive bacterium *Escherichia coli* and the gram negative bacterium *Lactobacillus casei* to the surface of the PDMSUr:HPW hybrid coatings and evaluated the resistance to biofilm formation [27]. The results showed that the PDMSUr:HPW coatings prevented the adhesion of both bacterias on the substrate surface. The evaluation of the rinsing solutions, that were used to remove bacteria that were poorly adhered to the substrate surface, suggested that the coatings were not bactericidal but bacteriostatic. This means, that the initial bacterial adhesion and consequently the

surface biofilm formation on the substrates were inhibited by the hybrid coatings. The underlying mechanism for this antibacterial action in the PDMSUr:HPW coatings is assumed to be a combination of factors. On the one hand, the superacid HPW [111, 113, 114] can transfer protons to the amino groups of unreacted APTES increasing the amount of positively charged nitrogen on the surface of the coating as probed by X-ray Photoelectron Spectroscopy. It can be assumed that the higher the amount of HPW, the higher is the percentage of protonated nitrogen species. The antibacterial capacity of PDMSUr may then arise from the electrostatic interaction between the positive charges of hybrid hydroxyurethane and the negative portions of the bacteria cell wall. On the other hand, the roughness of the PDMSUr:HPW films presented a Ra parameter near 0.077 μm up to 0.150 μm while for the uncoated substrates the corresponding values were higher than

0.20 μm . As demonstrated by Medilanski *et al.*, microbial adhesion on linear surfaces is minimal when the roughness parameter Ra is smaller than 0.16 [115]. Hence, the bacteriostatic behaviour can also be related to the reduced roughness.

Only recently, we tested the antimicrobial activities of self-supported membranes of PDMSUr:H₃PO₄ hybrids. For that purpose, PDMSUr:H₃PO₄ membranes were tested by inoculation with *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermides* ATCC 0128) and methicillin-resistant *S. aureus* ATCC -N315 (MRSA). The experimental details are given in the Electronic Supplementary Materials. The results (Table S1) reveal a bacteriostatic action of PDMSUr:H₃PO₄ against *S. aureus* and MRSA bacteria as well as the bactericidal activity against *S. epidermides*. The biostatic property was also observed for the extract of the hybrid membrane, even after seven days of immersion in Brain Heart Infusion broth. It can be

Figure 10 Representation of the percentage of growth of the strains tested in the different membranes.

assumed that some PDMSUr:H₃PO₄ minor compounds, such as residual precursors, protons, or phosphate, are delivered into the medium. This antimicrobial activity of PDMSUr:H₃PO₄ against relevant bacteria encouraged us to investigate further this material as wound dressing or adhesive for biomedical devices uses. For this reason, additional medically relevant, pathogenic yeasts and fungi were selected and evaluated in terms of susceptibility to PDMSUr:H₃PO₄ membranes. In particular, the filamentous fungus *Aspergillus fumigatus* and the yeasts *Candida albicans*, *Candida glabrata*, *Cryptococcus neoformans* and *Cryptococcus gatti* were considered. Details on the performed assays are shown in the electronic supplementary materials. Our results suggest that PDMSUr:H₃PO₄ is a broad-spectrum antimicrobial agent. Growth inhibition was achieved for all the fungal pathogens currently reported as leading agents of both nosocomial infections and persistence in different medical devices (Figure 10). Noteworthy, the PDMSUr:H₃PO₄ used as growth substrate showed biostatic activity against the *A. fumigatus* and *C. glabrata* while biocide activity was observed against *C. albicans*, *C. neoformans*, and *C. gatti*. These results point out the promising use of PDMSUr:H₃PO₄ membranes as a control strategy against multiple pathogens. It is furthermore worthy to notice, that the mechanism of action of this biomaterial

was broad enough to support either the growth inhibition or cell death of microorganisms regardless of their genetic traits or whether they are multi drug resistant or intrinsically tolerant to clinically used drugs. In addition, our results reveal that the combination of PDMSUr and H₃PO₄ accounts for the observed antimicrobial properties since none of the precursor compounds—except the H₃PO₄—showed antimicrobial activity (see Table S2 and associated methodology in the Electronic Supplementary Materials). As a first trail to explain the biocidal effect of PDMSUr:H₃PO₄, we investigated the time dependent pH value of the culture medium as well as of purified water films, which were in contact with the hybrid membrane. Table S3 shows that in contrast to other cases that we studied before [116], no acidulation was observed. More details are presented in the Section 2 of the Electronic Supplementary Materials.

For applicability in medical devices, the compatibility to human cells must be considered. For this reason, the PDMSUr materials were assessed for biocompatibility with osteoblast and fibroblast cells via WST-1 methodology. The cell viabilities results are shown in Figure 11. According to the specifications of the ISO 10993-5 standard (see also Section 3 in the Electronic Supplementary Materials for method details), which considers a material toxic when the reduction of the viable cells is more than

30%, the urethanesil materials with both HPW, as reported in Ref. [27], and H_3PO_4 presented here present no cytotoxic effect after 24 h of extraction. Nonetheless, further tests are required to evaluate the cytotoxicity effects of PDMSur: H_3PO_4 after extended extraction time.

4.3 Photonic Applications

Considering all the highlighted applications of the PDMSur-based materials, the optic and photonic potentials applications are still underexploited. To the best of our knowledge, the first factual report pointing out the light emitting utilizations of siloxane-based materials was published in 2017 by Liu *et al.* [117]. In their work, they considered

poly(tetramethyldisiloxane)hydroxyurethanes (PTMDSHU) and observed that the hydroxyurethane unit of linear polyhydroxyurethane acts as an effective photoluminescent (PL) chromophore. The PL profile and quantum yields can be tuned by properly choosing the linker between

the hydroxyurethane moieties, which also affects the chain conformation. Under optimized conditions, they were able to demonstrate the potential use as white light with low voltage and high luminance.

Exploiting the revealed PL profile from the PTMDSHU unit, Xu *et al.* [118] developed a Fe^{3+} sensor based on PTMDSHU obtained from chemical fixation of CO_2 into 1,3-bis-(3-glycidoxypopyl) tetramethyldisiloxane, which was posteriorly reacted with 1,6-diaminohexane to yield a fluorescent PTMDSHU material. The obtained materials present PL quenching when exposed in Fe^{3+} rich environments. The proposed mechanism considers that Fe^{3+} chelate with carbonyl and secondary amine to form complexes, which in turn increased the UV absorption. The lower detection limit of Fe^{3+} was calculated to be $4.56 \mu\text{M}$.

The PL effect of hybrid urethanesil materials was also demonstrated by L.D.

Figure 11 Cytotoxicity of PDMSUr materials in comparison with the positive (PC) and negative (NC) controls. ^aData taken from Ref. [27]

Carlos and co-workers [119], who prepared sol-gel derived hybrids polyethylene glycol repeated units grafted onto a siliceous backbone. They demonstrated that the white light PL arises from an unusual convolution of a longer-lived emission that originates in NH groups with shorter lived electron-hole recombination occurring in the siliceous domains.

Based on the synthetic procedure discussed above, in our group we considered longer siloxane chains to prepare the silicone-urethane hybrid using IPDA as linker and APTES as chain termination agents [24] and loaded the PDMSUr with an Eu^{3+} polyoxometalate (POM) complex, hereafter referred to as PDMSUr:EuPOM. The Eu^{3+} was incorporated into the PDMSUr during the aminolysis step [26] by using $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$, a sandwich bis-lacunary Keggin compound [120]. For the obtained material, white light generation was observed upon UV irradiation. As shown in Figure 12, the colour coordinates at intersection were determined within the white light region ($x = 0.313$ and $y = 0.332$). Moreover, a suitable colour rendering index (CRI) of 61 and colour correlated temperature (CCT) of 4888K (neutral white light) was found. The PDMSUr:EuPOM material does have the capacity of white light luminescence with the benefits of utilization of mild conditions, easy processability, self-standing flexible films as well as self-adhesive coatings. It is

Figure 12 Calculated colour coordinates for the PDMSUr:EuPOM in the CIE 1931 colour diagram. Inset: digital photograph of the film under UV exposure, showing the white light generation. Figure was taken from Ref. [26].

worthy to notice that the specific colour coordinates were not only due to the rare earth fluorescence but due to its combination with the urethanesil matrix. This highlights the contribution of the hybrid material toward this photonic behaviour.

4. Conclusions

In this review, we presented hybrid urethanesils obtained by using sol-gel approach and carbon dioxide fixation as a substitute for isocyanate in the traditional route to produce polyurethanes. Using CO_2 makes the synthesis strategy a possible contribution to negative emission approaches and is therefore, a contribution to a more environmental-friendly future. The synthesis methods,

some properties, and potential applications of these materials were presented. The hydroxyurethane hybrids are versatile, highly adherent and self-adhesive materials that can be obtained as sticky gels, elastomers, and self-supported films.

We summarized recent studies and pointed out to what extent the hybrid PDMSUr materials are superior to common PU materials, especially for the application as coatings. We provide examples of how the pristine PDMSUr material can yield water-repellent coatings due to the hydrophobic properties of the PDMS building block in the polymer structure. Moreover, we demonstrated three possibilities on how new functionalities can be applied to such materials. By using phosphoric acid or phosphotungstic acid as hydrolysis-condensation catalysts, it was possible to achieve antimicrobial properties against relevant pathogens associated with nosocomial or healthcare-associated infections. Furthermore, a flexible white light emission platform and a polyvalent anti-corrosion coating in biological fluid and acid or basic media for titanium alloys or stainless steel were reported. We argue that further development of these versatile materials alongside with a deeper understanding of the structure-property relationships can widen their application possibilities

Based on these recent developments, we conclude that the class of PDMSUr is a

multifunctional platform of auspicious hybrid materials. Upon advanced innovation associated processes, PDMSUr may contribute to more sustainable industrial activities. Nevertheless, it is important to emphasize that innovation “is the process whereby any scientific discovery or invention or idea is converted to a commercial product, process or service”, as Landau put it in 1998 [121]. Thus, the PDMSUr hybrid technology has still a long way to go.

Conflict of Interest: The authors declare that they have no conflict of interest.

Acknowledgements

The authors would like to thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the grants 2011/06019-0, 2013/05279-3, 2011/08120-0, 2018/19785-1, and 2018/15670-5. Furthermore, the support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the grants 302185/2017-8 is acknowledged, as well as the German Academic Exchange Service (DAAD) for grant 57210526. Further thanks go to the joint PROBRAL program between Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and DAAD for grant 8881.198673/2018-01 for fostering the Brazilian-German bilateral collaboration.

References

1. Sharmin E, Zafar F (2012) Polyurethane: An Introduction. In:

- Polyurethane. InTech, pp 3–16
2. Cornille A, Auvergne R, Figovsky O, et al (2017) A perspective approach to sustainable routes for non-isocyanate polyurethanes. *Eur Polym J* 87:535–552. <https://doi.org/10.1016/j.eurpolymj.2016.11.027>
 3. Akindoyo JO, Beg MDH, Ghazali S, et al (2016) Polyurethane types, synthesis and applications – a review. *RSC Adv* 6:114453–114482. <https://doi.org/10.1039/C6RA14525F>
 4. Biesmans G (2010) The Global Polyurethane Market. In: Randall D, Lee S (eds) *The Huntsmann Polyurethanes Book*. John Wiley & Sons, Everberg, pp 9–22
 5. Sanchez C, Rozes L, Ribot F, et al (2010) “Chimie douce”: A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *Comptes Rendus Chim* 13:3–39. <https://doi.org/10.1016/j.crci.2009.06.001>
 6. Bello D, Herrick CA, Smith TJ, et al (2007) Skin Exposure to Isocyanates: Reasons for Concern. *Environ Health Perspect* 115:328–335. <https://doi.org/10.1289/ehp.9557>
 7. Kathalewar MS, Joshi PB, Sabnis AS, Malshe VC (2013) Non-isocyanate polyurethanes: from chemistry to applications. *RSC Adv* 3:4110. <https://doi.org/10.1039/c2ra21938g>
 8. Blattmann H, Fleischer M, Bähr M, Mülhaupt R (2014) Isocyanate- and Phosgene-Free Routes to Polyfunctional Cyclic Carbonates and Green Polyurethanes by Fixation of Carbon Dioxide. *Macromol Rapid Commun* 35:1238–1254. <https://doi.org/10.1002/marc.201400209>
 9. Maisonneuve L, Lamarzelle O, Rix E, et al (2015) Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s. *Chem Rev* 115:12407–12439. <https://doi.org/10.1021/acs.chemrev.5b00355>
 10. Bossion A, Jones GO, Taton D, et al (2017) Non-Isocyanate Polyurethane Soft Nanoparticles Obtained by Surfactant-Assisted Interfacial Polymerization. *Langmuir* 33:1959–1968. <https://doi.org/10.1021/acs.langmuir.6b04242>
 11. Rockström J, Schellnhuber HJ, Hoskins B, et al (2016) The world’s biggest gamble. *Earth’s Futur* 4:465–470. <https://doi.org/10.1002/2016EF000392>
 12. Aresta M (2010) *Carbon Dioxide as Chemical Feedstock*. Wiley
 13. Duraccio V, Gnani MG, Elia V (2015) Carbon capture and reuse in an industrial district: A technical and economic feasibility study. *J CO2 Util* 10:23–29. <https://doi.org/10.1016/j.jcou.2015.02.004>
 14. Beniah G, Uno BE, Lan T, et al (2017) Tuning nanophase separation behavior in segmented polyhydroxyurethane via judicious choice of soft segment. *Polymer (Guildf)* 110:218–227. <https://doi.org/10.1016/j.polymer.2017.01.017>

15. Beniah G, Heath WH, Torkelson JM (2017) Functionalization of hydroxyl groups in segmented polyhydroxyurethane eliminates nanophase separation. *J Polym Sci Part A Polym Chem* 55:3347–3351. <https://doi.org/10.1002/pola.28722>
16. Pan WC, Lin C-H, Dai SA (2014) High-performance segmented polyurea by transesterification of diphenyl carbonates with aliphatic diamines. *J Polym Sci Part A Polym Chem* 52:2781–2790. <https://doi.org/10.1002/pola.27302>
17. Figovsky O, Leykin A, Shapovalov L (2016) NON-ISOCYANATE POLYURETHANES – YESTERDAY, TODAY AND TOMORROW. *Altern Energy Ecol* 3–4:95–108. <https://doi.org/10.15518/isjaee.2016.03-04.009>
18. Figovsky O, Beilin D (2013) *Advanced Polymer Concretes and Compounds*. CRC Press
19. Figovsky OL, Shapovalov L, Leykin A, et al (2013) Progress in Elaboration of Nonisocyanate Polyurethanes Based on Cyclic Carbonates. *Int Lett Chem Phys Astron* 3:52–66. <https://doi.org/10.18052/www.scipress.com/ILCPA.3.52>
20. Pilch-Pitera B (2014) Polyurethane powder coatings containing polysiloxane. *Prog Org Coatings* 77:1653–1662. <https://doi.org/10.1016/j.porgcoat.2014.05.021>
21. Henderson CMB (1987) *Structural Chemistry of Silicates; Structure, Bonding and Classification*. *Earth-Science Rev* 24:154–155. [https://doi.org/10.1016/0012-8252\(87\)90019-5](https://doi.org/10.1016/0012-8252(87)90019-5)
22. Willerth S (2017) *Engineering Neural Tissue from Stem Cells*. Elsevier
23. Liu C (2015) Development of Anti-fouling Coating Using in Marine Environment. *Int J Environ Monit Anal* 3:373. <https://doi.org/10.11648/j.ijema.20150305.30>
24. Aguiar KR, Santos VG, Eberlin MN, et al (2014) Efficient green synthesis of bis(cyclic carbonate) poly(dimethylsiloxane) derivative using CO₂ addition: a novel precursor for synthesis of urethanes. *RSC Adv* 24334–24343. <https://doi.org/10.1039/c4ra03846k>
25. Rossi de Aguiar KMF, Alves VS, Noeske P-LM, et al (2019) Hybrid films based on nonisocyanate polyurethanes with antimicrobial activity. In: *Materials for Biomedical Engineering*. Elsevier, pp 77–116
26. Simões MB, Ullah S, Hazra C, et al (2018) Eco-friendly polydimethylsiloxane-based self-supporting film containing europium-polyoxometalate: A flexible luminescent material for white light generation. *J Lumin* 201:384–389. <https://doi.org/10.1016/j.jlumin.2018.04.041>
27. Rossi de Aguiar KMF, Nascimento M V., Faccioni JL, et al (2019) Urethanes PDMS-based: Functional hybrid coatings for metallic dental implants. *Appl Surf Sci* 484:1128–1140. <https://doi.org/10.1016/j.apsusc.2019.04.058>
28. Rossi de Aguiar KMF, Specht U, Maass JF, et al (2016) Surface modification by physical treatments on biomedical grade metals to

- improve adhesion for bonding hybrid non-isocyanate urethanes. RSC Adv 6:47203–47211. <https://doi.org/10.1039/C6RA05397A>
29. Rossi De Aguiar KMF, Ferreira-Neto EP, Blunk S, et al (2016) Hybrid urethanesil coatings for inorganic surfaces produced by isocyanate-free and sol-gel routes: Synthesis and characterization. RSC Adv 6:19160–19172. <https://doi.org/10.1039/c5ra24331a>
 30. de Aguiar KR, Rischka K, Gätjen L, et al (2018) Biomimetic PDMS-hydroxyurethane terminated with catecholic moieties for chemical grafting on transition metal oxide-based surfaces. Appl Surf Sci 427:166–175. <https://doi.org/10.1016/j.apsusc.2017.08.142>
 31. Lima EF de S, Imasato H, Cavaleiro ETG, et al (2019) Effect of hydroxyapatite nanoparticles silanization on the preparation of nanocomposites of Hydroxyurethane polydimethylsiloxane with hydroxyapatite. In: Encontro da Sociedade Brasileira de Pesquisa em Materiais - SBPMat. Sociedade Brasileira de Pesquisa em Materiais - SBPMat
 32. Bayer O (1947) Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane). Angew Chemie. <https://doi.org/10.1002/ange.19470590901>
 33. Boiteux G, Cuvé L, Pascault JP (1994) Synthesis and properties of polyurethanes based on polyolefin: 3. Monitoring of phase separation by dielectric relaxation spectroscopy of segmented semicrystalline polyurethane prepared in bulk by the use of emulsifiers. Polymer (Guildf). [https://doi.org/10.1016/0032-3861\(94\)90068-X](https://doi.org/10.1016/0032-3861(94)90068-X)
 34. Urbano J, Manzarbetia F, Caramelo C (2008) Cholesterol Embolism Evaluated by Polarized Light Microscopy after Primary Renal Artery Stent Placement with Filter Protection. J Vasc Interv Radiol 19:189–194. <https://doi.org/10.1016/j.jvir.2007.10.006>
 35. St. John KR (2014) The use of polyurethane materials in the surgery of the spine: a review. Spine J 14:3038–3047. <https://doi.org/10.1016/j.spinee.2014.08.012>
 36. Usman A, Zia KM, Zuber M, et al (2016) Chitin and chitosan based polyurethanes: A review of recent advances and prospective biomedical applications. Int J Biol Macromol 86:630–645. <https://doi.org/10.1016/j.ijbiomac.2016.02.004>
 37. Korthagen NM, Brommer H, Hermesen G, et al (2019) A short-term evaluation of a thermoplastic polyurethane implant for osteochondral defect repair in an equine model. Vet J 251:105340. <https://doi.org/10.1016/j.tvjl.2019.105340>
 38. de Vita R, Buccheri EM, Villanucci A, Pozzi M (2019) Breast Reconstruction Actualized in Nipple-sparing Mastectomy and Direct-to-implant, Prepectoral Polyurethane Positioning: Early Experience and Preliminary Results. Clin Breast Cancer 19:e358–e363.

- <https://doi.org/10.1016/j.clbc.2018.12.015>
39. Alves P, Ferreira P, Gil MH (2012) Biomedical polyurethanes-based materials. In: Polyurethane: Properties, Structure and Applications. Nova Publishers New York, pp 1–25
 40. Ghasemlou M, Daver F, Ivanova EP, Adhikari B (2019) Bio-based routes to synthesize cyclic carbonates and polyamines precursors of non-isocyanate polyurethanes: A review. *Eur Polym J* 118:668–684. <https://doi.org/10.1016/j.eurpolymj.2019.06.032>
 41. Tersac G (2007) Chemistry and technology of polyols for polyurethanes. Milhail Ionescu. Rapra Technology, Shrewsbury, UK. *Polym Int* 56:820–820. <https://doi.org/10.1002/pi.2159>
 42. Zia KM, Anjum S, Zuber M, et al (2014) Synthesis and molecular characterization of chitosan based polyurethane elastomers using aromatic diisocyanate. *Int J Biol Macromol*. <https://doi.org/10.1016/j.ijbiomac.2014.01.073>
 43. Engels H-W, Pirkel H-G, Albers R, et al (2013) Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges. *Angew Chemie Int Ed* 52:9422–9441. <https://doi.org/10.1002/anie.201302766>
 44. Cypryk M, Apeloig Y (2002) Mechanism of the Acid-Catalyzed Si–O Bond Cleavage in Siloxanes and Siloxanols. A Theoretical Study. *Organometallics* 21:2165–2175. <https://doi.org/10.1021/om011055s>
 45. Fugel M, Hesse MF, Pal R, et al (2018) Covalency and Ionicity Do Not Oppose Each Other-Relationship Between Si–O Bond Character and Basicity of Siloxanes. *Chem - A Eur J* 24:15275–15286. <https://doi.org/10.1002/chem.201802197>
 46. Weinhold F, West R (2011) The Nature of the Silicon–Oxygen Bond. *Organometallics* 30:5815–5824. <https://doi.org/10.1021/om200675d>
 47. Gillespie RJ, Johnson SA (1997) Study of Bond Angles and Bond Lengths in Disiloxane and Related Molecules in Terms of the Topology of the Electron Density and Its Laplacian. *Inorg Chem* 36:3031–3039. <https://doi.org/10.1021/ic961381d>
 48. KICKELBICK G (2006) Hybrid Materials. Wiley
 49. Whan Cho J, Il Sul K (2001) Characterization and properties of hybrid composites prepared from poly(vinylidene fluoride–tetrafluoroethylene) and SiO₂. *Polymer (Guildf)* 42:727–736. [https://doi.org/10.1016/S0032-3861\(00\)00371-2](https://doi.org/10.1016/S0032-3861(00)00371-2)
 50. Kim K-M, Adachi K, Chujo Y (2002) Polymer hybrids of functionalized silsesquioxanes and organic polymers utilizing the sol–gel reaction of tetramethoxysilane. *Polymer (Guildf)* 43:1171–1175. [https://doi.org/10.1016/S0032-3861\(01\)00732-7](https://doi.org/10.1016/S0032-3861(01)00732-7)
 51. Wen J, Wilkes GL (1996) Organic/Inorganic Hybrid Network Materials by the Sol–Gel Approach. *Chem Mater* 8:1667–1681. <https://doi.org/10.1021/cm9601143>

52. Pavličević J, Špirková M, Jovičić M, et al (2019) Structure—Functional property relationship of aliphatic polyurethane-silica hybrid films. *Prog Org Coatings* 126:62–74. <https://doi.org/10.1016/j.porgcoat.2018.10.011>
53. He Z, Gao T, Duan D, Soucek MD (2019) Effect of mixed sol-gel precursors on inorganic-organic polyurethane hybrid thermosets: DOE study. *Prog Org Coatings*. <https://doi.org/10.1016/j.porgcoat.2019.04.023>
54. Alasti Bonab S, Moghaddas J, Rezaei M (2019) In-situ synthesis of silica aerogel/polyurethane inorganic-organic hybrid nanocomposite foams: Characterization, cell microstructure and mechanical properties. *Polymer (Guildf)* 172:27–40. <https://doi.org/10.1016/j.polymer.2019.03.050>
55. Son S-J, Kim K-B, Lee Y-H, et al (2011) Effect of acrylic monomer content on the properties of waterborne poly(urethane-urea)/acrylic hybrid materials. *J Appl Polym Sci* 124:n/a–n/a. <https://doi.org/10.1002/app.35662>
56. Athawale VD, Kulkarni MA (2009) Preparation and properties of urethane/acrylate composite by emulsion polymerization technique. *Prog Org Coatings* 65:392–400
57. Ping T, Zhou Y, He Y, et al (2016) Preparation and characterization of yellowing resistance and low volume shrinkage of fluorinated polysiloxane urethane acrylate. *Prog Org Coatings* 97:74–81. <https://doi.org/10.1016/j.porgcoat.2016.03.023>
58. Cakić SM, Valcic MD, Ristić IS, et al (2019) Waterborne polyurethane-silica nanocomposite adhesives based on castor oil-recycled polyols: Effects of (3-aminopropyl)triethoxysilane (APTES) content on properties. *Int J Adhes Adhes* 90:22–31. <https://doi.org/10.1016/j.ijadhadh.2019.01.005>
59. Kreye O, Mutlu H, Meier MAR (2013) Sustainable routes to polyurethane precursors. *Green Chem* 15:1431. <https://doi.org/10.1039/c3gc40440d>
60. Joshi M, Adak B, Butola BS (2018) Polyurethane nanocomposite based gas barrier films, membranes and coatings: A review on synthesis, characterization and potential applications. *Prog Mater Sci* 97:230–282. <https://doi.org/10.1016/j.pmatsci.2018.05.001>
61. Błażek K, Datta J (2019) Renewable natural resources as green alternative substrates to obtain bio-based non-isocyanate polyurethanes-review. *Crit Rev Environ Sci Technol* 49:173–211. <https://doi.org/10.1080/10643389.2018.1537741>
62. Ghasemlou M, Daver F, Ivanova EP, Adhikari B (2020) Synthesis of green hybrid materials using starch and non-isocyanate polyurethanes. *Carbohydr Polym* 229:115535. <https://doi.org/10.1016/j.carbpol.2019.115535>
63. Suryawanshi Y, Sanap P, Wani V (2019) Advances in the synthesis of non-isocyanate polyurethanes. *Polym Bull* 76:3233–3246. <https://doi.org/10.1007/s00289->

- 018-2531-7
64. Datta J, Włoch M (2016) Progress in non-isocyanate polyurethanes synthesized from cyclic carbonate intermediates and di- or polyamines in the context of structure–properties relationship and from an environmental point of view. *Polym Bull* 73:1459–1496. <https://doi.org/10.1007/s00289-015-1546-6>
 65. Heilig ML (1994) United States Patent Office. ACM SIGGRAPH Comput Graph 28:131–134. <https://doi.org/10.1145/178951.178972>
 66. Zabalov M V, Tiger RP, Berlin AA (2012) Mechanism of urethane formation from cyclocarbonates and amines: a quantum chemical study. *Russ Chem Bull* 61:518–527. <https://doi.org/10.1007/s11172-012-0076-8>
 67. Zabalov M V, Levina MA, Krashennnikov VG, Tiger RP (2014) Bifunctional catalysis by acetic acid in the urethane formation from cyclocarbonates and amines: quantum chemical and kinetic study. *Russ Chem Bull* 63:1740–1752. <https://doi.org/10.1007/s11172-014-0662-z>
 68. Tomita H, Sanda F, Endo T (2001) Model reaction for the synthesis of polyhydroxyurethanes from cyclic carbonates with amines: Substituent effect on the reactivity and selectivity of ring-opening direction in the reaction of five-membered cyclic carbonates with amine. *J Polym Sci Part A Polym Chem* 39:3678–3685. <https://doi.org/10.1002/pola.10009>
 69. Günther F, Batista Simões M, Imasato H, Pereira Rodrigues-Filho U (2019) Experimental and theoretical assessment of the aminolysis of cyclo carbonate to form polyhydroxyurethanes. *Mater Today Commun* 21:100604. <https://doi.org/10.1016/j.mtcomm.2019.100604>
 70. Lambeth RH, Rizvi A (2019) Mechanical and adhesive properties of hybrid epoxy-polyhydroxyurethane network polymers. *Polymer (Guildf)* 183:121881. <https://doi.org/10.1016/j.polymer.2019.121881>
 71. Sukumaran Nair A, Cherian S, Balachandran N, et al (2019) Hybrid Poly(hydroxy urethane)s: Folded-Sheet Morphology and Thermoreversible Adhesion. *ACS Omega* 4:13042–13051. <https://doi.org/10.1021/acsomega.9b00789>
 72. North M, Pasquale R, Young C (2010) Synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem* 12:1514. <https://doi.org/10.1039/c0gc00065e>
 73. Martín C, Fiorani G, Kleij AW (2015) Recent Advances in the Catalytic Preparation of Cyclic Organic Carbonates. *ACS Catal* 5:1353–1370. <https://doi.org/10.1021/cs5018997>
 74. Subramaniam A, Sethuraman S (2014) Biomedical Applications of Nondegradable Polymers. In: *Natural and Synthetic Biomedical Polymers*. Elsevier, pp 301–308
 75. Schindler WD, Hauser PJ (2004) *Chemical finishing of textiles*. Woodhead Publishing Limited

76. Ben Soltane H, Roizard D, Favre E (2013) Effect of pressure on the swelling and fluxes of dense PDMS membranes in nanofiltration: An experimental study. *J Memb Sci* 435:110–119.
<https://doi.org/10.1016/j.memsci.2013.01.053>
77. Stefanis E, Panayiotou C (2008) Prediction of hansen solubility parameters with a new group-contribution method. *Int J Thermophys* 29:568–585.
<https://doi.org/10.1007/s10765-008-0415-z>
78. Belmares M, Blanco M, Goddard W a., et al (2004) Hildebrand and hansen solubility parameters from molecular dynamics with applications to electronic nose polymer sensors. *J Comput Chem* 25:1814–1826.
<https://doi.org/10.1002/jcc.20098>
79. Bahri S, Jonsson CM, Jonsson CL, et al (2011) Adsorption and surface complexation study of L-DOPA on rutile (α -TiO₂) in NaCl solutions. *Environ Sci Technol* 45:3959–3966.
<https://doi.org/10.1021/es1042832>
80. Grunwald I, Rischka K, Kast SM, et al (2009) Mimicking biopolymers on a molecular scale: nano(bio)technology based on engineered proteins. *Philos Trans R Soc A Math Phys Eng Sci* 367:1727–1747.
<https://doi.org/10.1098/rsta.2009.0012>
81. Zdyb A, Krawczyk S (2016) Characterization of adsorption and electronic excited states of quercetin on titanium dioxide nanoparticles. *Spectrochim Acta Part A Mol Biomol Spectrosc* 157:197–203.
<https://doi.org/10.1016/j.saa.2016.01.006>
82. Liu G, Wu G, Huo S, et al (2017) Synthesis and properties of non-isocyanate polyurethane coatings derived from cyclic carbonate-functionalized polysiloxanes. *Prog Org Coatings* 112:169–175.
<https://doi.org/10.1016/j.porgcoat.2017.07.013>
83. Lana SLB, Seddon AB (1998) X-Ray Diffraction Studies of Sol-Gel Derived ORMOSILs Based on Combinations of Tetramethoxysilane and Trimethoxysilane. *J Sol-Gel Sci Technol* 13:461–466.
<https://doi.org/10.1023/A:1008685614559>
84. Moreno EM, Levy D (2000) Role of the Comonomer GLYMO in ORMOSILs As Reflected by Nile Red Spectroscopy. *Chem Mater* 12:2334–2340.
<https://doi.org/10.1021/cm001048e>
85. Brennan JD, Hartman JS, Ilnicki EI, Rakic M (1999) Fluorescence and NMR Characterization and Biomolecule Entrapment Studies of Sol-Gel-Derived Organic-Inorganic Composite Materials Formed by Sonication of Precursors. *Chem Mater* 11:1853–1864.
<https://doi.org/10.1021/cm9910097>
86. Ferreira-Neto EP, Ullah S, Ysnaga OAE, Rodrigues-Filho UP (2014) Zn²⁺ doped ormosil–phosphotungstate hybrid films with enhanced photochromic response. *J Sol-Gel Sci Technol* 72:290–300.
<https://doi.org/10.1007/s10971-014-3404-7>
87. Frenkel-Mullerad H, Ben-Knaz R,

- Avnir D (2014) Preserving the activity of enzymes under harsh oxidizing conditions: Sol-gel entrapped alkaline phosphatase exposed to bromine. *J Sol-Gel Sci Technol* 69:453–456. <https://doi.org/10.1007/s10971-013-3226-z>
88. Cuéllar-Franca RM, Azapagic A (2015) Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. *J CO2 Util* 9:82–102. <https://doi.org/10.1016/j.jcou.2014.12.001>
 89. Rubio F, Rubio J, Oteo JL (2000) Effect of TiO₂ on the pore structure of SiO₂-PDMS ormosils. *J Sol-Gel Sci Technol*. <https://doi.org/10.1023/A:1008704701204>
 90. Almeida JC, Wacha A, Gomes PS, et al (2016) PDMS-SiO₂-TiO₂-CaO hybrid materials – Cytocompatibility and nanoscale surface features. *Mater Sci Eng C* 64:74–86. <https://doi.org/10.1016/j.msec.2016.03.071>
 91. Doro FG, Ramos AP, Schneider JF, et al (2014) Deposition of organic–inorganic hybrid coatings over 316L surgical stainless steel and evaluation on vascular cells. *Can J Chem* 92:987–995. <https://doi.org/10.1139/cjc-2014-0034>
 92. Rodrigues-Filho UP, de Aguiar KMF, Rischka K (2015) Processo De Obtenção De Materiais Derivados De Polidimetilsiloxano (Pdms) Materiais Derivados De Polidimetilsiloxano (Pdms) E Seus Usos. 62
 93. Mackenzie JD, Bescher E (2003) Some factors governing the coating of organic polymers by sol-gel derived hybrid materials. *J Sol-Gel Sci Technol* 27:7–14. <https://doi.org/10.1023/A:1022659323517>
 94. Wu Y, Guo P, Zhao Y, et al (2019) Hydrophobic, transparent waterborne polyurethane-polydimethylsiloxane composites prepared from aqueous sol-gel process and applied in corrosion protection. *Prog Org Coatings* 127:231–238. <https://doi.org/10.1016/j.porgcoat.2018.06.002>
 95. Aguiar KMFR de (2015) Síntese de hidroxietileno-poli (dimetilsiloxano) com diferentes terminações de cadeia via fixação de CO₂: síntese, caracterizações e potenciais aplicações. Universidade de São Paulo
 96. Ferreira-Neto EP, de Carvalho FLS, Ullah S, et al (2013) Surface structure and reactivity study of phosphotungstic acid-nitrogenated ormosils. *J Sol-Gel Sci Technol* 66:363–371. <https://doi.org/10.1007/s10971-013-3018-5>
 97. Souza AL, Marques LA, Eberlin MN, et al (2012) Self-assembled hybrid films of phosphotungstic acid and aminoalkoxysilanes on SiO₂/Si surfaces. *Thin Solid Films* 520:3574–3580. <https://doi.org/10.1016/j.tsf.2011.12.069>
 98. Leroy F, Miró P, Poblet JM, et al (2008) Keggin Polyoxoanions in Aqueous Solution: Ion Pairing and Its Effect on Dynamic Properties by Molecular Dynamics Simulations. *J*

- Phys Chem B 112:8591–8599.
<https://doi.org/10.1021/jp077098p>
99. Marcus Y (2009) Effect of Ions on the Structure of Water: Structure Making and Breaking. *Chem Rev* 109:1346–1370.
<https://doi.org/10.1021/cr8003828>
 100. Ball P, Hallsworth JE (2015) Water structure and chaotropicity: their uses, abuses and biological implications. *Phys Chem Chem Phys* 17:8297–8305.
<https://doi.org/10.1039/C4CP04564E>
 101. Collins KD, Neilson GW, Enderby JE (2007) Ions in water: Characterizing the forces that control chemical processes and biological structure. *Biophys Chem* 128:95–104.
<https://doi.org/10.1016/j.bpc.2007.03.009>
 102. Costa AO, Oliveira LB, Lins MPE, et al (2013) Sustainability analysis of biodiesel production: A review on different resources in Brazil. *Renew Sustain Energy Rev* 27:407–412.
<https://doi.org/10.1016/j.rser.2013.06.005>
 103. Thangaraj B, Solomon PR, Muniyandi B, et al (2019) Catalysis in biodiesel production—a review. *Clean Energy* 3:2–23.
<https://doi.org/10.1093/ce/zky020>
 104. Mousdale D (2008) Diversifying the Biofuels Portfolio. In: *Biofuels*. CRC Press, Boca Raton, pp 285–320
 105. Danaei SM, Safavi A, Rooinpeikar SMMM, et al (2011) Ion release from orthodontic brackets in 3 mouthwashes: An in-vitro study. *Am J Orthod Dentofac Orthop* 139:730–734.
<https://doi.org/10.1016/j.ajodo.2011.03.004>
 106. Morais LS De, Guimarães GS, Elias CN (2007) Liberação de íons por biomateriais metálicos. *Rev Dent Press Ortod e Ortop Facial* 12:48–53. <https://doi.org/10.1590/S1415-54192007000600006>
 107. Nuevo-Ordóñez Y, Montes-Bayón M, Blanco-González E, et al (2011) Titanium release in serum of patients with different bone fixation implants and its interaction with serum biomolecules at physiological levels. *Anal Bioanal Chem* 401:2747–2754.
<https://doi.org/10.1007/s00216-011-5232-8>
 108. Yang X., Vang C, Tallman D., et al (2001) Weathering degradation of a polyurethane coating. *Polym Degrad Stab* 74:341–351.
[https://doi.org/10.1016/S0141-3910\(01\)00166-5](https://doi.org/10.1016/S0141-3910(01)00166-5)
 109. Kowalczyk K, Łuczka K, Grzmil B, Szychaj T (2012) Anticorrosive polyurethane paints with nano- and micro-sized phosphates. *Prog Org Coatings* 74:151–157.
<https://doi.org/10.1016/j.porgcoat.2011.12.003>
 110. Yang XF, Tallman DE, Bierwagen GP, et al (2002) Blistering and degradation of polyurethane coatings under different accelerated weathering tests. *Polym Degrad Stab* 77:103–109.
[https://doi.org/10.1016/S0141-3910\(02\)00085-X](https://doi.org/10.1016/S0141-3910(02)00085-X)
 111. Drago RS, Dias JA, Maier TO (1997) An Acidity Scale for Brønsted Acids Including H₃PO₄. *J Am Chem Soc* 119:7702–7710.
<https://doi.org/10.1021/ja9639123>
 112. Dhivya S, Padma VV, Santhini E (2015) Wound dressings – a review. *BioMedicine* 5:22.

- <https://doi.org/10.7603/s40681-015-0022-9>
113. Fu S, Chu J, Chen X, et al (2015) Well-Dispersed H₃PO₄/SiO₂ Nanoparticles on Mesoporous Polymer for Highly Efficient Acid-Catalyzed Reactions. *Ind Eng Chem Res* 54:11534–11542. <https://doi.org/10.1021/acs.iecr.5b03385>
 114. Essayem N, Frety R, Coudurier G, Vedrine JC (1997) Ammonia adsorption-desorption over the strong solid acid catalyst H₃PO₄ and its Cs⁺ and NH₄⁺ salts Comparison with sulfated zirconia. *J Chem Soc - Faraday Trans* 93:3243–3248. <https://doi.org/10.1039/a701097d>
 115. Medilanski E, Kaufmann K, Wick LY, et al (2002) Influence of the Surface Topography of Stainless Steel on Bacterial Adhesion. *Biofouling* 18:193–203. <https://doi.org/10.1080/08927010290011370>
 116. Piva RH, Rocha MC, Piva DH, et al (2018) Acidic Dressing Based on Agarose/Cs_{2.5}H_{0.5}PO₄ Nanocomposite for Infection Control in Wound Care. *ACS Appl Mater Interfaces* 10:30963–30972. <https://doi.org/10.1021/acsami.8b09066>
 117. Liu B, Wang YL, Bai W, et al (2017) Fluorescent linear CO₂-derived poly(hydroxyurethane) for cool white LED. *J Mater Chem C*. <https://doi.org/10.1039/c7tc01236e>
 118. Xu W, Liu B, Cai X, et al (2018) Fluorescent poly(hydroxyurethane): Biocompatibility evaluation and selective detection of Fe(III). *J Appl Polym Sci* 135:46723. <https://doi.org/10.1002/app.46723>
 119. Carlos LD, Sá Ferreira RA, De Zea Bermudez V, Ribeiro SJL (2001) Full-Color Phosphors from Amine-Functionalized Crosslinked Hybrids Lacking Metal Activator Ions. *Adv Funct Mater* 11:111–115. [https://doi.org/10.1002/1616-3028\(200104\)11:2<111::AID-ADFM111>3.0.CO;2-V](https://doi.org/10.1002/1616-3028(200104)11:2<111::AID-ADFM111>3.0.CO;2-V)
 120. Neves CS, Granadeiro CM, Cunha-Silva L, et al (2013) Europium polyoxometalates encapsulated in silica nanoparticles - Characterization and photoluminescence studies. *Eur J Inorg Chem* 2013:2877–2886. <https://doi.org/10.1002/ejic.201201482>
 121. Landau R (1998) The Process of Innovation in the Chemical Industry. In: Arora A, Landau R, Rosenberg N (eds) *Chemicals and Long-Term Economic Growth. Insights from the Chemical Industry*. John Wiley & Sons Inc, New York, USA, pp 139–180