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# SILICONES THROUGH TIME: GLOBAL MILESTONES AND THE IAŞI SCIENTIFIC SCHOOL'S ACHIEVEMENTS

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*This paper is dedicated to the memory of Dr. Mihai Marcu (1936–2020)*

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Silicones represent a unique class of materials that have become indispensable in everyday life and in almost all areas of human activity – from medicine and cosmetics, to construction, electronics, energy and transportation (including space). The paper reviews the essential stages of the discovery and development of silicones, briefly explaining their structural peculiarities that give them special properties, such as thermal stability, flexibility and resistance in extreme conditions. In this context, the important contributions of research carried out in Romania in this field are presented, from the beginnings to current directions, in accordance with international trends. The latter include the development of dielectric silicone elastomers for applications in sensors, actuators (including for soft robotics) and generators; new organosilicon compounds, of interest for their biological, optical, electrical, magnetic or surface properties; their metal complexes; as well as efforts to recycle silicone materials. The review attempts to provide an accessible and current picture of the major role that silicones play in the technological progress and sustainability of modern society.

*Keywords*: silicones, organosilicon compounds, silicone applications, silicone recycling, Romanian research contributions.

## 1. SILICON AND SILICONES: FROM DISCOVERY TO CUTTING-EDGE APPLICATIONS

Silicon, first isolated and described in 1824 by Jöns Jacob Berzelius [7], is the second most abundant element in the Earth's crust, surpassed only by oxygen [63]. After establishing its character and properties as an element, attention turned to its compounds, especially organosilicon ones. The discovery by Frederic Stanley Kipping in 1927 of siloxane polymers, also generically named by him as silicones, and the Rochow-Muller direct synthesis of methylchlorosilanes in 1940, one of the

best-known industrial processes for obtaining organosilicon compounds (Fig. 1a), launched the silicones industry, which soon delivered a wide range of products. They conquered almost all areas of human activity, making silicones the revelation of the second half of the 20th century, while, at the beginning of the 21st century, silicones became the first choice for soft robotics.

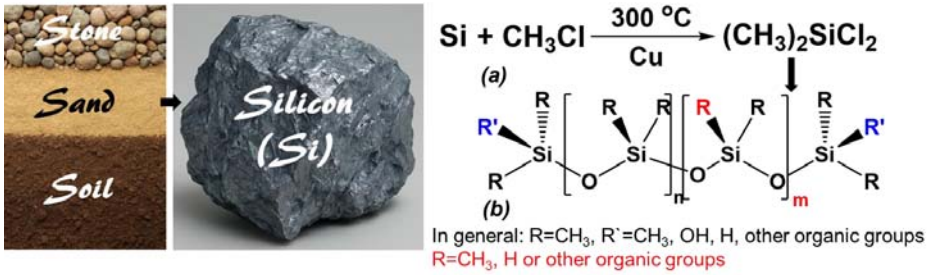


Figure 1. The chemical path from sand to polysiloxanes.

At the same time, as a result of the development of methods for obtaining high-purity silicon, suitable for electronic devices, since 1960 silicon itself has become the standard material for semiconductors, Silicon Valley taking its name from this material with a fundamental role in microelectronics and computers [69, 29].

Silicones are based on longer or shorter polyorganosiloxane chains, in which silicon atoms are connected alternately with oxygen atoms in linear or cross-linked structures, and the free valences of silicon are completed by organic groups (Fig. 1b, 2a). The Si–O bond, with an average length of 1.64 ± 0.03 Å, is shorter than the sum of the atomic radii, which is attributed to a partial double bond character due to the pπ–dπ interaction between oxygen and silicon. At the same time, the electronegativity difference between the silicon atom (≈1.8) and oxygen (≈3.5) imparts the Si–O bond a partial ionic character of about 50% [32,34,58]. These factors also give the siloxane bond a high bond energy, around 450 kJ/mol, higher than that of C–C (≈350 kJ/mol) and C–O (≈360 kJ/mol) bonds, explaining the thermal and chemical resistance, as well as the exceptional durability of silicone compounds [27]. The siloxane bond is also distinguished by the large Si–O–Si angle and the low rotational energy, which give the siloxane chain remarkable flexibility (Fig. 2a) [62]. The bond size and the siloxane angle are influenced by the nature of the substituents. The predominant organic substituent on silicon atoms is the highly hydrophobic methyl group which significantly influences the properties of silicones.

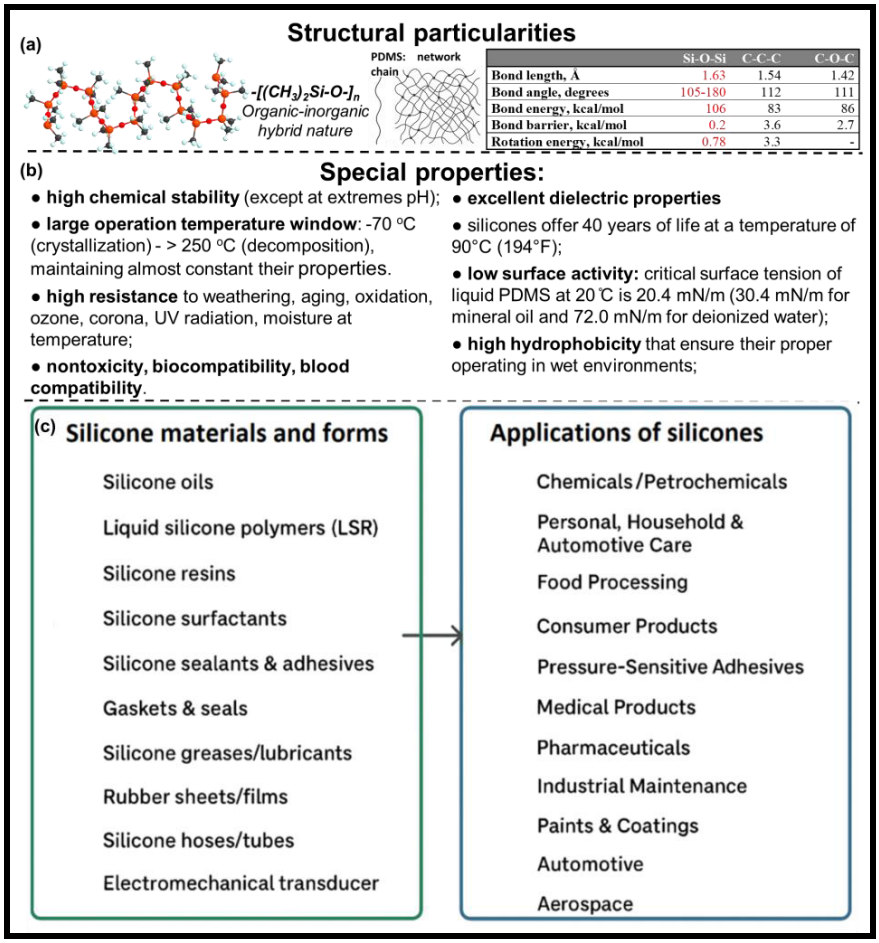


Figure 2. (a) Structural features; (b) representative properties;
(c) forms and applications of silicones.

The peculiarities of the siloxane bond and angle and the nature of the groups attached to the silicon atoms give silicones their own characteristics, different from those of carbon-based polymers, such as high thermal, chemical, environmental and aging resistance, high hydrophobicity and low surface tension, biological inertness, optical transparency, UV and oxygen plasma resistance, easy processability, etc. (Fig. 2b), which makes them useful in many fields. Thus, based on these properties, silicones have come to form the basis of a huge range of products and applications covering all sectors of human activity, from medicine to aerospace (Fig. 2c). Although they emerged after organic polymers, at a time when polymer science was already well established, silicones rapidly found applications

in areas where organic materials failed to perform. Beyond the gaskets and coatings used on various spacecraft components, even the sole of the boot that left Neil Armstrong's historic footprint on the Moon in 1969 was made of silicon [64].

In the last years, the silicone materials industry has made significant progress, driven by technological innovations, ecological requirements, and the diversification of applications. Currently, the silicone industry is advancing through automation, the use of artificial intelligence and 3D printing, improved quality control, production efficiency, and product precision. The development of more sustainable materials and the adoption of eco-friendly practices lead to reduced waste and environmental impact. These innovations are essential for competitiveness and for adapting to the increasingly demanding requirements of the modern market [66]. According to the Global Silicone Market Report 2025 published by The Business Research Company [66], the global silicone market reached a value of USD 24.65 billion in 2024 and is projected to reach USD 48.71 billion by 2029, with a compound annual growth rate (CAGR) of 14.5%, evaluated by product type (elastomers, fluids, gels, other product types), applications (construction, transportation, electrical and electronics, textiles, personal care and pharmaceuticals, other applications), and by end user (industrial, electronics, machinery, aerospace, medical).

The main players in the silicone market are: KCC Corporation (South Korea), GELEST, INC. (U.S.), NuSil Technology LLC (U.S.), Shin-Etsu Chemical Co., Ltd. (Japan), Wacker Chemie AG (Germany), Dow Corning Corporation (U.S.), Momentive (U.S.), Elkem Silicones (Norway), Evonik Industries (Germany), Specialty Silicones Products, Inc. (U.S.), Saint-Gobain Performance Plastics (France), BASF SE (Germany) [71].

## 2. THE BEGINNINGS OF SILICONE RESEARCH IN ROMANIA

Against the backdrop of global recognition of macromolecular chemistry – initiated as early as the 1920s by Hermann Staudinger's seminal research on the macromolecular structure of rubber, cellulose, and resins, and acknowledged through his Nobel Prize in 1953 [65] – the newly established Institute of Chemistry in Iași (founded in 1949 and later renamed the "Petru Poni" Institute of Macromolecular Chemistry, ICMPP, in 1964) focused its research on this innovative field from its very first years.

In the context of the spectacular progress of organic polymers, which revolutionized the synthetic fiber, plastics, and elastomer industries, the first efforts in the synthesis and application of silicone polymers were also emerging worldwide, valued for their chemical and thermal stability as well as their specialized uses in electronics, construction, and medicine.

Within this scientific and industrial climate, nationally, research groups dedicated to polymer chemistry were formed, developing both fundamental studies

on polymers and applied research aimed at creating technologies for classes of monomers and polymers, including silicones. Thus, ICMPP early on aligned itself with the international trend of modernizing chemistry, becoming a recognized center for its original and applied contributions to polymer science and technology.

Research in the field of silicones began in the early 1970s when, through the national research plan, several research centers in Romania, including ICMPP, were assigned the task of developing technologies for silicone production and implementing them at the chemical platform in Borzești. Conditions were created, within the possibilities at that time, to support this effort (equipment, supply of material resources, travel in the country, and occasionally even abroad). However, being an emerging field, access to scientific information was largely restricted, as it was generally protected by patents.

Within the Inorganic Polymers Laboratory at ICMPP, which focused on silicones and was the only one to continue this endeavor and to maintain research in this domain up to the present, each stage of the process or product (silicone monomers, polymers, oils, resins, emulsions, greases, elastomers) had dedicated infrastructure and a team consisting of researchers, engineers, and technicians. Well-established collaboration protocols existed between ICMPP, the specialists and the working group at the Borzești platform, and the Institute of Technological Engineering and Design for the Chemical Industry (IITPIC) but also with other relevant institutions to carry out this endeavor. There was also some openness to international collaboration and knowledge exchange. In July 1988, a team of researchers from the Inorganic Polymers Laboratory at ICMPP carried out a technical visit to a silicone company in Jilin, China, regarding silicone-related issues. In 1989, a collaboration was initiated between the Romanian Academy and the German Academy, involving the „P. Poni" Institute of Macromolecular Chemistry in Iași and the Institute of Physical Chemistry in Berlin, regarding studies on optimizing the synthesis of methylchlorosilanes.

During the period 1970–1989, in the Laboratory of Inorganic Polymers at ICMPP, technological processes were developed at both laboratory (Fig. 3f) and pilot scale for the production of silicones: pilot technology for the production of heat-cured methyl silicone rubber (1986); pilot technology for the production of demulsifying silicone emulsions (1986); pilot technology for the production of methylchlorosilanes (1987); pilot technology for the production of demulsifying methyl silicone oils with viscosities of 50–1000 cSt (1987); pilot technology for the production of antifoaming silicone emulsions (1987); pilot technology for the production of heat-cured methylvinyl silicone rubber (1987) (Fig. 3e). All these technologies were reviewed and approved by the relevant specialized commissions of that time.

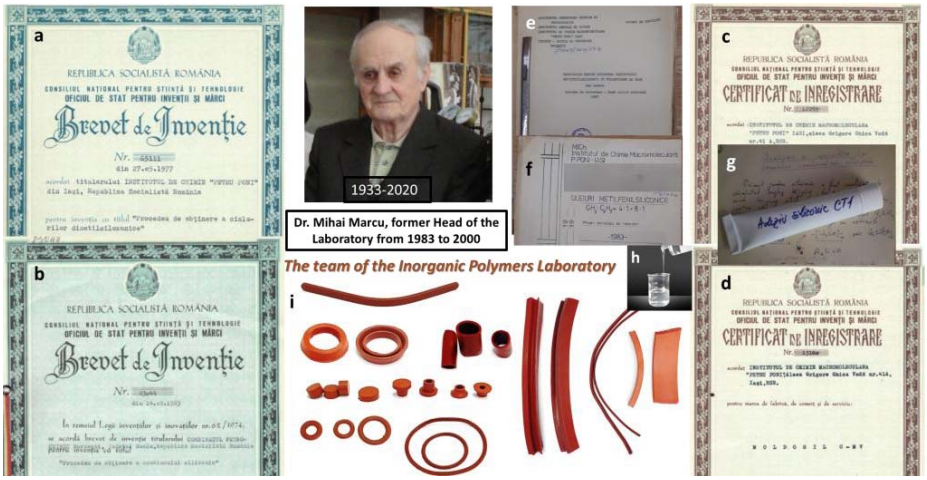


Figure 3. Image fragments from patent certificates, trademarks, technological documentation, and examples of silicone products: (a) Patent No. 65111/1977 – Process for obtaining dimethylsiloxane cycles; (b) Patent No. 83044/1983 – Process for obtaining silicone rubber; (c,d) Silicone trademarks Moldosil CT-1 and CM-V; (e) Technology for producing methylvinyl silicone rubber with hot vulcanization (pilot-scale research, 1987); (f) Laboratory process for methylphenylsilicone oils (1983); (g) Silicone adhesive Moldosil CT-1, based on room-temperature-vulcanizing polydimethylsiloxanes, shown over a 1980 draft manuscript by Dr. Mihai Marcu reviewing silicone rubbers; (h) Polydimethylsiloxane; (i) Selected silicone samples produced at ICMPP at micro-production scale before 1990.

During that period, more than 40 patents were granted by the State Office for Inventions and Trademarks for various silicone products and processes for their production (Fig. 3a, b), as well as trademarks for silicone products generically known as Moldosil (Fig. 3c, d). These refer to: demulsifying methylsilicone oils, MOLDOSIL UMD –50, 100, 350, 5000, 1000 Cst; hot-curing methylsilicone rubbers, MOLDOSIL CM-40, 50, 60, 70, 80O ShA; hot-curing methylvinylsilicone rubber, MOLDOSIL CMV-40, 50, 60, 70, 80O Sh A; room-temperature-curing silicone rubber, single-component adhesive, MOLDOSIL Ct-1; room temperature vulcanizing silicone rubber, two-component molding, MOLDOSIL Ct-2; demulsifying methylsilicone emulsion, MOLDOSIL ED-35, 60; defoaming methylsilicone emulsion, MOLDOSIL EA-10, 15, 20; demulsifying methylsilicone emulsion, MOLDOSIL ED-35, 60; Defoaming methylsilicone emulsion, MOLDOSIL EA-10, 15, 20.

At ICMPP, a pilot plant for the production of methylchlorosilanes and a micro-production unit were operational, where cyclosiloxanes, siloxane polymers (Fig. 3h), oils, silicone adhesive (Fig. 3g), silicone rubbers, and various products based on these materials (Fig. 3i) were produced. The coordination of these

researches was ensured during that period by Dr. Aglaia Ciobanu, followed by Dr. Mihai Marcu.

## 3. RECENT APPROACHES IN SILICONES RESEARCH

The major changes that occurred after 1989 in Romania, which led to the collapse of the industry, affected, among others, the approach to implementing a national silicone industry. The liberalization of imports led to a decrease in interest in Romanian products, which, being made only on a small scale, were generally more expensive. This led to the rapid loss of industry interest in the development of this field. As a result, research in the field of silicones focused on fundamental aspects, addressing reaction mechanisms and optimizing methods for the synthesis of polysiloxanes, including the use of artificial intelligence tools [17,18,33], chemical modification [43] and their processing [4,56] for specific applications, such as materials for dental linings [12] or lumbar disc prostheses [45,46], adhesives for post-seismic emergency strengthening of buildings [14], mechatronics [5], etc. At the same time, research has focused on the development of new siloxane-organic hybrid compounds and materials, especially siloxane-organic copolymers (*e.g.*, with polyurethane, polyamide, polystyrene, polyacrylates, cellulose, polysulfone, cyclodextrines, chitosan, etc., as the organic component), copolymers with different internal functions (ether, ester, silyl-ether, silyl-ester, carbonate, sulfone, azomethine, etc.) [1,8,9,11,21,24,25,31,35–37,44,47,48,51], as well as on the preparation of silicone-organic composites (*e.g.* silicone/lignin [51]) or silicone-inorganic composites (generally silicone/metal oxides, ceramics, clays powders [10]). The combination of silicones with various organic or inorganic components has been carried out in order to develop new compounds and materials, study their properties and identify their application potential, for example as surfactants for obtaining nanoparticles or encapsulation of various components [42], or nanostructured materials [13].

On the other hand, recent research has brought significant advances not only in the functional properties of silicones but also in their processing. In the Department of Inorganic Polymers at ICMPP, fully silicone-based formulations suitable for 3D printing technology have been developed (Fig. 4) [57]. These formulations enable the customized fabrication of objects with complex architectures, which are of interest for fields such as microelectronics, smart materials, and bioengineering, where complex and adaptable structures are essential.

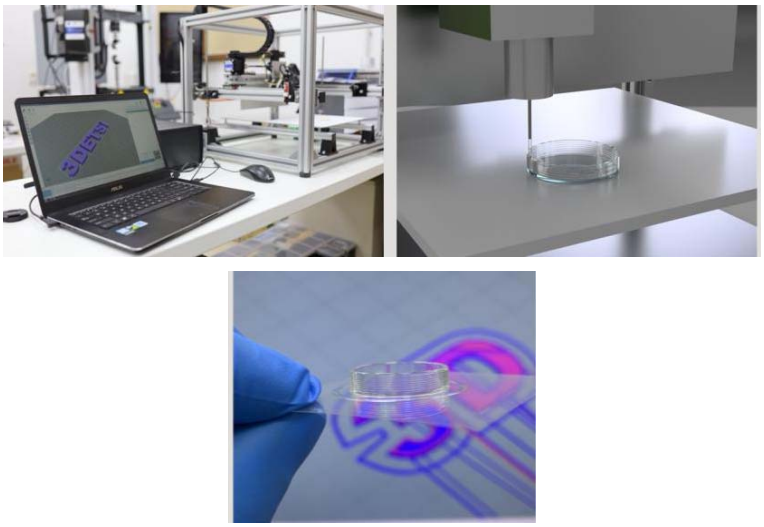

Figure 4. Illustration of the 3D printing technology for fully silicone-based formulations developed at ICMPP in 2023 [57]

All of this has led to an increase in the number of publications on the topic of silicones. An analysis of the Web of Science database using the keywords ‘silicone’, ‘siloxane’, and ‘silane’ for Romanian-affiliated publications up to 2025 reveals the leading role of ICMPP among national research centers and universities (Fig. 5).

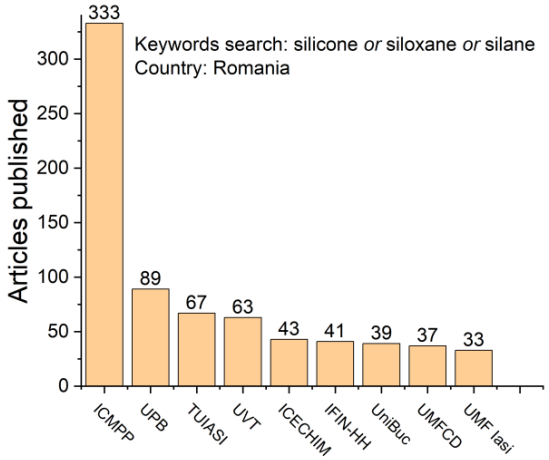


Figure 5. Number of publications on silicones by Romanian research centers and universities up to 2025 (October, 15).

### 3.1. SILICONE ELASTOMERS AS ACTIVE MATERIALS

Starting in 2008, at ICMPP, silicone elastomers–previously developed as passive materials for support, protection, coating, transport, sealing, lubrication, etc. – began to be investigated from the perspective of their 'smart' capabilities, *i.e*., ability to respond to electrical and mechanical stimuli.

Electroactive polymers are known generically as "artificial muscles". Devices based on such polymers that must be dielectric, called electromechanical transducers, and which consist in principle of a dielectric elastomer film with compliant electrodes applied on both sides, are able to change their shape and size (*e.g*. contraction in thickness and expansion in plane) when an electric field is applied to them, functioning as actuators (Fig. 6a). Worldwide, systematic research on electroactive polymers began in the 1990s, after the contributions of R. Perline and was further stimulated in 1999 when Y. Bar-Cohen challenged the scientific community to develop a robotic arm actuated by artificial muscles based on these polymers [2]. Several types of elastomers (natural rubber, acrylic, polyurethanes, silicones, etc.) were approached in this aim, silicone elastomers, consisting in principle of polydimethylsiloxanes or polydimethylsiloxanes chemically modified with various organic groups, or with various physical additions, proved to be between favorites.

Electroactive polymers can also function as sensors (transform deformation into an electrical signal) and generators (energy accumulated during deformation is released as electrical energy after removal of the force) [6]. The performance of such an electromechanical transducer mainly depends on several key factors: the quality of the dielectric (evaluated by permittivity, dielectric strength, Young's modulus and stability in different media), the quality of the electrode and its compliance with the dielectric. Most research is aimed at improving these parameters through different approaches.

The first results at ICMPP were published in 2009 on polydimethylsiloxane/ silica/pyrite elastomer composites [10]. This was followed by other articles (over 50 to date) reporting own results obtained in the effort to improve the electromechanical performances of dielectric silicone elastomers [3,4,15,38–41, 55–57]. In this direction, a series of research projects have been implemented and collaborations have been developed with teams from both Romania and abroad (for example, EMPA-Dübendorf, Switzerland; DTU-Denmark; Scuola Superiore Sant'Anna di Pisa, Italy).

Reasonable performances were obtained, at the level of those reported in the literature for other superior elastomers in terms of some of the characteristics (dielectric permittivity, for example): 30-layer stacked transducer that can lift 250 times its weight at 20 V/μm [55]; actuator with 85% out-of-plane deformation at an applied electric field of 450 V/μm [6]; generator with dielectric film (diameter 120 mm, thickness 150 μm) and electrode (diameter 30 mm) based on elastomeric silicone composites (with $BaTiO_3$, respectively CB) that can convert mechanical energy into electrical energy with an efficiency of 8.84%) [14].

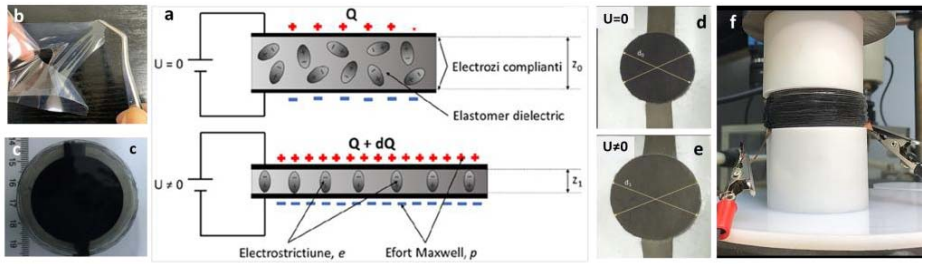


Figure 6. (a) Operating principles for a dielectric elastomer actuator; (b) ICMPP laboratory-prepared silicone elastomer films and (c) actuator; (d) actuator at rest; (e) actuator under applied voltage; (f) stacked actuator capable of lifting weights or damping mechanical shocks.

### 3.2. INTEGRATION OF SILICONE MOIETIES INTO METAL-CONTAINING ARCHITECTURES

In 2010, based on several exploratory studies, the group began a systematic research on coordination compounds with ligands containing silane or siloxane segments. This initiative leveraged the team's existing expertise and, in the early stages, benefited from the conceptual and methodological guidance of a recognized specialist in metal complex chemistry – Acad. Constantin Turtă from the Institute of Chemistry in Chisinau.

This created an arc over time of about 60 years, considering that, at the beginnings of the institute, under the leadership of Acad. Radu Cernătescu (1951–1958), the research was primarily focused on coordination compounds and was carried out in the same laboratory, which later became the Laboratory of Inorganic Polymers.

The lack of intermolecular interactions between chains makes polydimethylsiloxane, which is the basis of silicones, amorphous and flowable even at very high molecular weights (over 1000 kDa). Partial replacement of methyl groups with other organic entities, capable of developing intermolecular interactions, or the introduction of such blocks into the siloxane chain can lead to an increase in the degree of ordering and chain rigidity, but most often phase separation occurs, a phenomenon that is otherwise useful for certain applications, especially in nanotechnology. But the best way to obtain highly ordered siloxane compounds is to attach coordinating groups and use them as ligands for metals. By this approach, metal complex structures of different dimensionalities (0D, 1D, 2D, 3D) have been obtained (Fig. 7). These constitute a remarkable class of compounds with special properties induced by the co-existence in the structure of the rigid and polar organic coordination block with the very flexible and hydrophobic silicone moiety [19,49,50,60]. Such compounds are hydrophobic in the solid state, soluble in nonpolar solvents and self-assembled in solution. Due to the demonstrated properties, some of these compounds are of interest in optics, catalysis, molecular spintronics.

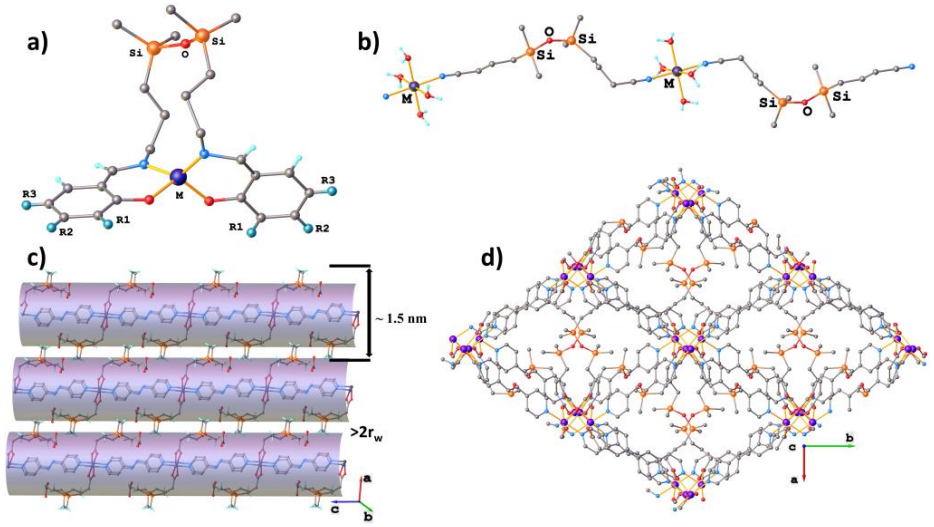


Figure 7. Representative examples of coordination structures with ligands containing siloxane moieties: (a) small molecular coordination compounds, 0D, $M^{2+}L^{2-}$ with L – salicylaldimine derived from 1,3-bis(3-aminopropyl)tetramethyldisiloxane and different substituted salicylaldehyde [19]; (b) one-dimensional, 1D, $\{[CyM(H_2O)_4](ClO_4)_2\}_n$ with Cy – 1,3-bis(cyanopropyl) tetramethyldisiloxane [50]; (c) two-dimensional, 2D, $(Cx^{2-}Zn^{2+}AzPy)_n$, with AzPy – 4,4′-azopyridine and Cx - 1,3-bis(3-carboxypropyl)tetramethyldisiloxane [60]; (d) three-dimensional, 3D, $\{[Mn_4(Cx)_3(etdipy)_5]\cdot 2ClO_4\}_n$ with Cx - 1,3-bis(3-carboxypropyl)tetramethyldisiloxane and Etdipy - 1,2-di(4-pyridyl)ethylene [49].

### 3.3. TOWARD SUSTAINABLE SILICONE MATERIALS

As shown in Fig. 2, silicones are notable for their long-term resistance under extreme conditions. However, as they reach the end of their useful life or deteriorate (cracks, scratches, wear, deformation, etc.), environmental impact issues arise. Although silicone waste is considered chemically and biologically stable, making it relatively safe for long-term landfill disposal, it is non-biodegradable and takes up significant space. Controlled disposal in specially designed sites, with leachate collection and soil protection, is recommended to minimize environmental impacts. Although this method is simple and cost-effective, it does not conserve resources and may pose long-term risks if impurities are present.

Global concerns about sustainability and the circular economy have also stimulated research on silicones, particularly from the perspective of reducing their high carbon footprint, which mainly arises from the metallurgical production of silicon. Recycling could reduce the impact of this step and increase the sustainability of silicone products. However, most silicones are covalently crosslinked, which

renders them thermosetting materials and poses particular challenges in recycling. For this reason, silicone recycling lags behind plastics, although significant progress has been made in recent years. Silicone recycling is approached through mechanical and chemical processes (Fig. 8), each with its advantages and limitations in terms of costs, energy consumption and $CO_2$ emissions.

Mechanical recycling of silicones involves grinding silicone waste and reusing it in the production of new materials, without altering their chemical structure. This method is considered environmentally friendly and cost-effective, as it requires less energy and fewer resources compared to chemical recycling. However, there are some drawbacks: the mechanical properties of recycled silicone may be reduced, limiting its use in high-performance applications, and proper sorting and cleaning of waste are necessary to maintain material quality, which can increase costs. Despite these challenges, mechanical recycling remains an effective approach for reducing waste and conserving resources [30]. Research by the ICMPP group in this field has focused on the cryomilling of silicone waste and the incorporation of the resulting powder into virgin silicone, yielding composites suitable for pressure sensors [53].

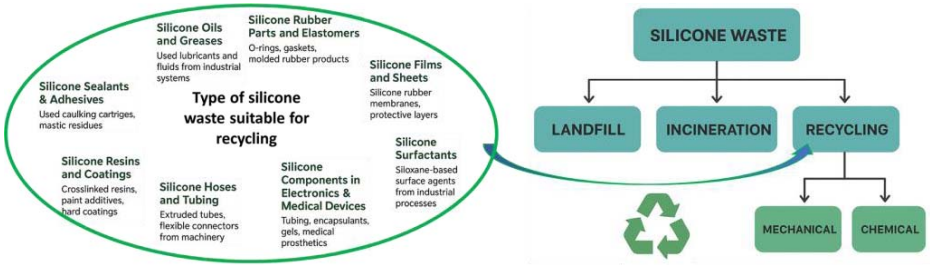


Figure 8. Examples of types of silicone waste and their management and recycling methods.

Chemical recycling of silicones involves breaking down (depolymerization) the material into its basic chemical components, which can then be reused to produce new silicone or other chemical products. This method allows the recovery of high-quality material comparable to virgin silicone and can handle complex or contaminated waste that cannot be mechanically recycled. While effective in conserving resources and reducing dependence on raw materials, chemical recycling is energy-intensive, costly, and requires specialized equipment and strict safety measures. The first developments in silicone recycling include the establishment of the ECO USA pilot plant, capable of processing around 6,000 tons of silicone materials annually through a chemical cracking method [73,74]. ECO USA is also expanding its capacity and product range to include emulsions, polymers, and other customized silicones [73–75]. A similar initiative has begun in Germany by New Dawn Silicones. This process involves heating silicone in large reactors with acid catalysts to break siloxane chains into dimethylcyclosiloxanes, which are then purified

and polymerized into high-quality silicone oils nearly equivalent to virgin materials but 10–15% cheaper [73]. Unlike mechanical recycling, chemical recycling preserves material quality, allows the production of customized silicone products, and offers significant environmental benefits, including an 8-ton reduction in $CO_2$ emissions per ton of recycled silicone and a 35% lower carbon footprint for the resulting PDMS compared to virgin material [61,67,68,70].

Very recently, a team of researchers at the French National Center for Scientific Research (CNRS)/CPE Lyon developed a chemical recycling process for silicone waste that converts any type of used silicone material (sealants, gels, adhesives, cosmetics, etc.) into silicon precursors such as methylchlorosilanes. The reported process allows the regeneration of silicones without loss of properties, effectively enabling "infinite" recycling [22,59].

At the laboratories of the "Petru Poni" Institute of Macromolecular Chemistry in Iași, studies are underway on the disintegration of silicones using the catalytic action of tetrabutylammonium fluoride (TBAF) and tetramethylammonium hydroxide (TMAH).

To make silicones more easily recyclable and self-healing, recent developments involve silicones crosslinked through dynamic, reversible bonds, so that the materials can be restored after damage (fractures, scratches, etc.) or at the end of their life and reused [20,23,54,72,28]. At ICMPP, ongoing research focuses on optimizing the production of recyclable silicones from functionalized polydimethylsiloxanes bearing amino and carboxyl groups capable of forming dynamic bonds [16].

## 4. CONCLUSION

The development of silicones at the global level has been remarkable, with these compounds becoming essential materials for technological and societal progress. In Romania, research in this field began with the ambitious goal of establishing a national silicone industry. Although historical events have interrupted the development of infrastructure and industrial capacities, a core of human resources with expertise in the field has remained at ICMPP to date. Capitalizing on the knowledge accumulated, Romanian researchers have continued to contribute to the field through fundamental studies, but with high applicative potential, and international collaborations, aligning themselves with current directions of global research. This continuity through knowledge confirms the sustainable potential of Romanian research in silicone chemistry.

**Acknowledgments**: The author gratefully thanks the pioneers who initiated this research at "Petru Poni" Institute of Macromolecular Chemistry in Iasi, all those who have advanced the field over time, and the current team (Department of Inorganic Polymers – DIP) who continue to carry it forward with dedication. The author thanks Dr. Codrin Țugui and Dr. Alexandru-Constantin Stoica for providing some of the images (Fig. 4–6) and structures (Figure 7) used in this review. Thanks to the Romanian Academy for funding the research activities of the institute..

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