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Polyurethane and rare-earth materials: a review

Materiais de poliuretanos e terras raras: uma revisão

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Abstract

Polyurethanes are polymers produced from polyols and isocyanates. Commonly, aiming to modify physicochemical properties of the resulting material, other chemical species can be introduced in the polymeric structure, modifying its mechanical, thermal and electronic characteristics and conferring more stability and resistance to external factors. The rare earth chemical elements, composed of lanthanides, Y and Sc, can give the materials such improved characteristics, and are still less researched when compared to other chemical elements. In the present study, a systematic search was carried out on the Web of Science platform. No studies were identified with polyurethanes and Sc, Pr, Pm, Sm, Dy and Ho, showing room for unexplored studies. Most of the articles investigated the luminescent characteristics of the chemical elements that were used, but it was also possible to notice trends in changing mechanical and thermal properties.

Keywords: Polyurethane. Rare-earth. Lanthanides.

Resumo

Os poliuretanos são polímeros produzidos a partir de polióis e isocianatos. Comumente, visando modificar as propriedades físico-químicas do material resultante, outras espécies químicas podem ser introduzidas na estrutura polimérica, modificando suas características mecânicas, térmicas e eletrônicas e conferindo maior estabilidade e resistência a fatores externos. Os elementos químicos das terras raras, compostos pelos lantanídeos, Y e Sc, podem conferir aos materiais características aprimoradas, sendo ainda menos pesquisados quando comparados a outros elementos químicos. No presente estudo, foi realizada uma busca sistemática na plataforma Web of Science. Não foram identificados estudos com poliuretanos e Sc, Pr, Pm, Sm, Dy e Ho, mostrando espaço para estudos inexplorados. A maioria dos artigos investigou as características luminescentes dos elementos químicos utilizados, mas também foi possível perceber tendências na mudança de propriedades mecânicas e térmicas.

Palavras-chave: Poliuretano. Terras raras. Lantanídeos.

1. Introduction

The rare-earth metals are a set composed of 17 chemical elements, being the lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), with atomic numbers between 57 and 71, plus the elements Sc and Y, with atomic numbers 21 and 39, respectively (Serra, 2011). Lanthanides have been known since 1787, through the discovery of the mineral gadolinite by the Swedish mineralogist Carl Axel Arrhenius (Serra *et al.*, 2015). The term "earths," on the other hand, was designated between the 18th and 19th centuries due to the nature of extraction of these elements, since they used the word "earth" to refer to metallic oxides in general, such as "alkaline earths”. On the other hand, the term "rare" refers to the place where such elements were found, initially in Sweden, and their separation is relatively complex. Thus, the "rare-earths" are not specifically earths, besides being relatively abundant (Sousa Filho & Serra, 2014), because these elements are widely distributed throughout the earth's crust, but in low concentrations (Serra *et al.*, 2015).

China has the largest rare earth reserves in the world, with more than 60% of the world's rare earths (Serra, 2011) besides being the largest producer of these elements, with 90% of the world supply (X. Yin *et al.*, 2021). In comparison, Brazil also stands out in relation to lanthanide reserves, since it has the third largest reserve of rare earth ores in the world, with 18%, however, its exploitation requires a significant investment for the raw material to have an added value as an end product (Carriello *et al.*, 2022; Sousa Filho & Serra, 2014).

According to Salfate and Sánches (2022) the chemical properties of rare earth elements are similar, for this reason they are treated as a group. The most common oxidation state provided for these elements is trivalent, although other states are known for certain elements. Within the rare earth groups, the lanthanides stand out due to the presence of the f layer, which is responsible for the luminescent properties of these materials, which have been highlighted in applications in several areas, such as biosensors and solar cells (Salfate & Sánchez, 2022; H. Zhang *et al.*, 2020). Rare earths can accrete several significant properties to the added matrix, such as flame retardancy. When adding to the rare earth in the matrix polymeric, it will confer a greater amount of solid inorganic residues that act as a barrier in the transfer of heat and mass, which delays the combustion phases of the material (Hobson *et al.*, 2022).

Other materials used in various segments of society are polyurethanes (PUs), plastic materials originated from the reaction between a chemical reagent with isocyanate groups and a substance rich in hydroxyls, called polyol. PUs have the final appearance of foam, rigid or flexible, extremely versatile (Alves *et al.*, 2021; Buzzi *et al.*, 2010), which can be applied in acoustic insulation, thermal insulation and in civil construction due to their excellent mechanical properties (Buzzi *et al.*, 2010; Mirza *et al.*, 2006; Somarathna *et al.*, 2018). PU’s can be produced through two main types of synthesis, namely the one-step method and the two-step method. The one-step method consists of mixing all the reagents at the same time, while the two-step method is based on the pre-reaction between an isocyanate and a diol, which will form a pre-polymer, which will later react with an extender of chain forming the polymer. Despite being an extremely versatile material, PU presents several challenges, such as petrochemical source reagents for its synthesis and high flammability, which are harmful to human health and the environment (Lima, 2007; C. Liu *et al*., 2021; Vahabi *et al*., 2020).

In order to further improve the properties of this material, various types of rare earth elements can be inserted into its structure, by virtue of their unique chemical, optical and magnetic characteristics due to their unique electronic structure, which have the ability to provide numerous attributes such as: increased thermal resistance, light radiation in the ultraviolet and magnetic properties (Chistoserdova, 2016; Fiedler *et al*., 2007; Mendes-Felipe *et al*., 2021; Y. Pan *et al*., 2020). In the light of the above, this paper aims to analyze through the Web of Science platform what are the main trends involving the properties and applications of all rare earth elements with polyurethane (PU).

2. Material and Methods

For the research we adapted the methodology of López-Belmonte *et al*. (2021), which uses Boolean operators to collect data from the Web of Science website (https://clarivate.com/webofsciencegroup/solutions/web-of-science) with the Boolean searchers: (polyurethane OR polyurethanes) AND (lanthanides OR lanthanide OR "rare earth" "rare earths" OR yttrium OR scandium OR lanthanum OR cerium OR praseodymium OR neodymium OR promethium OR samarium OR europium OR gadolinium OR terbium OR dysprosium OR holmium OR terbium OR thulium OR ytterbium OR lutetium). The survey was executed on September 16, 2022.

Subsequently, the analysis was performed according to Bearman *et al*. (2012). Firstly, the articles were categorized in relation to the rare earth element addressed in the work and how the production of these articles occurred as a function of time. Subsequently, each work was analyzed regarding the precursors used, materials formed, and properties studied. Property classifications were created according to Carlomagno and Rocha (2016), which relate:

> a) there must be clear rules about the limits and definition of each category; b) the categories must be mutually exclusive (what is in one category cannot be in another); c) the categories should be homogeneous (not have things that are very different from each other in the same group); d) it is necessary that the categories exhaust the possible content (no more content [...] that does not fit in any category); e) the classification must be objective, enabling replication of the study (Carlomagno & Rocha, 2016, p. 184).

3. Results and Discussion

After the search, 207 results were obtained. Subsequently, those that were duplicates, that did not present reports of research involving PU with a rare earth element in its structure, and those for which the full version was not available at the CAPES Portal de Periódicos were excluded. Thus, the inclusion criteria were papers that reported works that investigated in a practical way PU structures with at least one rare earth element, being this final structure in composite form or not. At the end of the process we obtained 80 articles that fit the scope, which were analyzed in their content. Only 2 papers were not available in full through the CAPES Periodical Portal, those being X.-H. Liu *et al*. (2006) and Mani and Jaganathan (2021).

Table 1 shows the categorization of the articles as to the rare earth element reported in the research. Since the paper may contain a report of research with more than one rare earth element, the same paper may be cited for two elements.

Table 1 - Selected works by rare earth element category.

Element	References of work with occurrence
Yttrium (Y)	(Albayrak *et al*., 2012; X. Chen *et al*., 2021; Ryszkowska *et al*., 2007; Saidi & Kadkhodayan, 2021; Yao *et al*., 2021)
Scandium (Sc)	-
Lanthanum (La)	(Chi *et al*., 2018; Gbur *et al*., 2013; Z. Liu *et al*., 2004; Lu *et al*., 2013; Macaskie *et al*., 2005; Y. Pan *et al*., 2020; Qian *et al*., 2020; Saidi & Kadkhodayan, 2021; Salazar-Muñoz *et al*., 2021; X. Shen *et al*., 2011; Xiao *et al*., 2017; Z. Yin *et al*., 2021; R. Yu *et al*., 2017)
Cerium (Ce)	(A. Saadat-Monfared & Mohseni, 2014; Anand & Sivaramakrishna, 2021; Baig & Khan, 2015; Bose *et al*., 2022; Ferrel-Álvarez *et al*., 2017; Fu *et al*., 2016; Huang *et al*., 2022; Jaganathan *et al*., 2022; Jorcin *et al*., 2010; Joshi *et al*., 2022; Mani *et al*., 2022; Martineau & Shek, 2006; Mastouri Mansourabad *et al*., 2020; Mo *et al*., 2019; Nguyen *et al*., 2021; Nhiem *et al*., 2018; Ni *et al*., 2021; Palma-Ramírez *et al*., 2017; G.-F. Pan *et al*., 2022; Roitti *et al*., 2004; Saadat-Monfared *et al*., 2012; Saha *et al*., 2019; Samardžija *et al*., 2022; Unnithan *et al*., 2014; S. Wang *et al*., 2019; Xavier, 2021; Xie *et al*., 2021; X. Yu *et al*., 2021, 2022)
Praseodymium (Pr)	-
Neodymium (Nd)	(R.-C. Liu *et al*., 2019; Mendes-Felipe *et al*., 2021; Yao *et al*., 2021)
Promethium (Pm)	-
Samarium (Sm)	-
Europium (Eu)	(Fiedler *et al*., 2007; Qian *et al*., 2021; Li *et al*., 2020; X. Wang *et al*., 2012; Jiang *et al*., 2013; Beltyukova & Balamtsarashvili, 1995; Z. Zhou *et al*., 2013; S. Zhou *et al*., 2007; Reisfeld *et al*., 2003; Ma *et al*., 2021; L. Gao *et al*., 2019; Basu & Vasantharajan, 2008; Saeed *et al*., 2005; Ilmi *et al*., 2019; Su, Zhang, Jia, Gao, Li, He, *et al*., 2019; W. Zhang *et al*., 2022; Xu *et al*., 2018; Garcia-Torres *et al*., 2014; Reisfeld *et al*., 2009; Reisfeld, 2004)
Gadolinium (Gd)	(Cai *et al*., 2020; Fiedler *et al*., 2007; X. Gao *et al*., 2022)
Terbium (Tb)	(Fiedler *et al*., 2007; Hilder *et al*., 2008; Reisfeld, 2004; Reisfeld *et al*., 2003; Rong *et al*., 2020; Ryszkowska *et al*., 2007; Su, Zhang, Jia, Gao, Li, Bai, *et al*., 2019; Suenaga *et al*., 2008; Sun *et al*., 2010; Villagra *et al*., 2021; J. Wang *et al*., 2013; Xi *et al*., 2017; Yang *et al*., 2022; W. Zhang *et al*., 2022)
Dysprosium (Dy)	-
Holmium (Ho)	-
Erbium (Er)	(Yao *et al*., 2021)
Thulium (Tm)	(Cai *et al*., 2020)
Ytterbium (Yb)	(Cai *et al*., 2020; Yao *et al*., 2021)
Lutetium (Lu)	(Zugle *et al*., 2011)

From the data in table 1 it is possible to quantify the occurrence of each rare earth element in the papers, as can be seen in figure 1.

Figure 1 - Occurence of Rare Earth Elements in Papers.

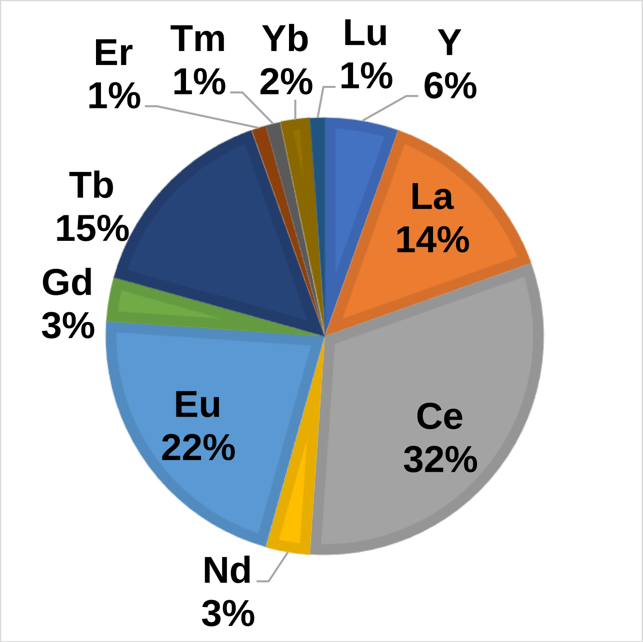
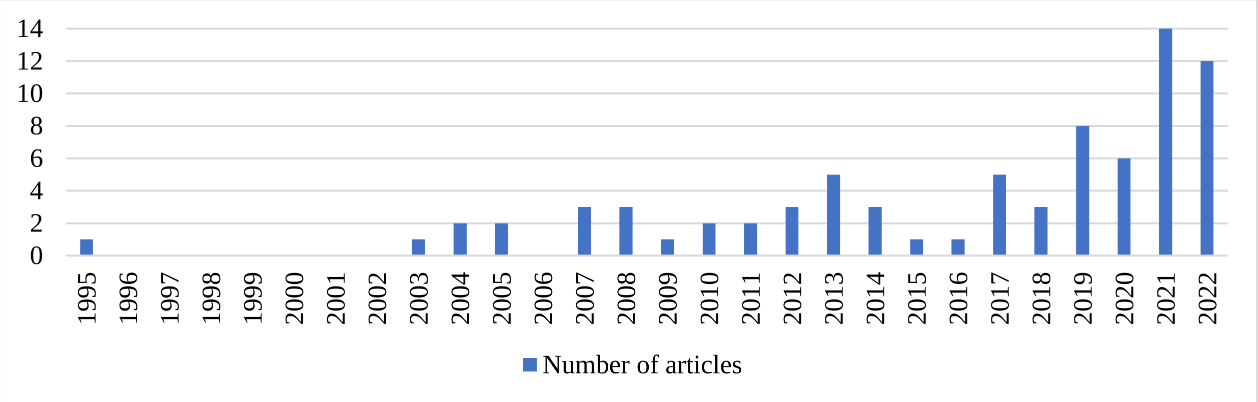


Figure 1 shows the predominance of the elements cerium, europium, lanthanum, and terbium, in that order. Lanthanum and cerium are the two most abundant rare earth elements in nature and most accessible on the market (Chakhmouradian & Wall, 2012; Ganguli & Cook, 2018), which may be an indicator of the high availability of these lanthanides. Europium and terbium, the second and fourth elements with the highest occurrence in the articles, have a higher price than lanthanum, lutetium and other rare earth elements. It should be noted that there has been a decrease in the prices of these two elements over the years (Chakhmouradian & Wall, 2012; Eggert *et al*., 2016; Ganguli & Cook, 2018). Possibly this price reduction occurred due to the potential applications that research has been indicating, especially those related to their luminescence properties (Dalal *et al*., 2022; Mohammadian *et al*., 2022; Q.-C. Wang *et al*., 2020).

Figure 2 shows the number of papers as a function of time. It can be seen that currently there is a growing interest in researching PU materials with earth elements, since the year with the highest occurrence of articles was in 2021 and the second in 2022. However, it should be noted that the present review was conducted in mid-2022, and the number of published papers may increase by the end of 2022.

Figure 2 - Numbers of articles involving polyurethane materials with rare earth elements published.



It is noteworthy that although prices for rare earths have decreased compared to the beginning of the century, increased demand and research in the fields has made modern society dependent on these materials (Song *et al*., 2021), these materials are mainly used in the production of ceramics, metal alloys and as catalysts (Ganguli & Cook, 2018). The fact that China is currently the largest exporter of rare earths and the crisis due to the pandemic caused by the spread of the SARS-COV-2 virus that causes COVID-19 disease have made the prices of rare earth elements volatile (Song *et al*., 2021), since they have specific properties, which in several cases cannot be replaced by other elements. This has led China, which holds the largest share of the market for these elements, to invest heavily in research in the area, in order to continue dominating this market (Y. Chen & Zheng, 2019). Such reasons explain why most of the authors of the papers arranged in table 1 are Chinese, and also the significant increase in research involving rare earths and PUs in the graphic in figure 2.

The categories used to classify the properties are shown in table 2, the number of papers found (N°) and the percentage in relation to the total number of papers (%). As a single article may have studied two or more properties, the sum of these percentages will not reach 100%.

Table 2 - Categories and classification of the articles according to the investigated properties.

Category	**Criterion of this category**	**N°**	**%**
Catalytic activity	Papers that studied the catalytic activity of the material.	2	3%
Bactericidal	Papers that studied how the material acts in the elimination of microorganisms.	1	1%
Biocompatibility	Papers that have studied how the material behaves in relation to biological tissues.	5	6%
Ionic Condutivity	Papers that have studied the ion conductivity in the material.	1	1%
Electromagnetic	Papers that studied the electromagnetic properties of the material.	6	8%
Hydrophobicity	Papers that studied the material's ability to repel water.	3	4%
Luminescence	Papers that have studied the luminescent properties of the material.	28	35%
Mechanical	Papers that studied the mechanical properties of the material.	11	14%
Optical properties	Papers that studied optical properties of the material, different from luminescence.	2	3%
Corrosion resistance	Papers that have studied how corrosion occurs in material when it is caused by non-mechanical actions.	6	8%
UV radiation resistance	Papers that have reported how the degradation of the material occurs by the action of ultraviolet radiation.	11	14%
Thermal Resistance	Papers that have studied how the material behaves with varying temperatures.	5	6%
Flame Retardancy	Papers that have reported how flame propagation occurs in the material.	7	9%
Sensorality	Papers that have studied how the material can detect a certain chemical species.	5	6%
None	Papers that did not report studies of some property of the material.	2	3%

Analyzing table 2 we notice the predominance of the three most investigated applications in the papers were luminescence, mechanical properties and UV radiation resistance, occurring in 35%, 14% and 14% of the articles, respectively. The predominance of papers with luminescence can be justified by the occurrence of rare earth elements, widely used for these explanations (Escudero *et al*., 2016; Ganguli & Cook, 2018; J. Shen *et al*., 2008). Ganguli and Cook (2018) also state that among the rare earth elements, lanthanum, cerium, europium, terbium and yttrium have several applications due to their luminescence. As it is noted in figure 1 that lanthanum, cerium, europium and terbium are the most studied, the 35% predominance of studies involving the luminescence property can be explained. The mechanical properties can be justified by the PU, as they are one of several characteristics of this material (Allami *et al.*, 2021; Kojio *et al.*, 2010; Vaidya *et al.*, 2022).

3.1. Polyurethanes with Y

Table 3 - Selected works involving polyurethane with yttrium.

Work	Final material	Property
(X. Chen et al., 2021)	Polyurethane composite with ytterbium citrate and ammonium polyphosphate.	Flame Retardancy
(Albayrak et al., 2012)	Yttrium-doped polyurethane/zirconia nanoparticle nanocomposite.	Electromagnetic
(Saidi & Kadkhodayan, 2021)	Polyanilide/polyurethane nanocomposite with yttrium nitrate and $La_{1.8}Sr_{0.2}Ni_{1-x}Co_xO_4$-$CaCu_3Ti_{4-x}Nb_xO_{12}$ $(0 < x < 1)$.	Electromagnetic
(Yao et al., 2021)	Polyurethane elastomer with carbon dots and yttrium chloride.	Luminescence
(Ryszkowska et al., 2007)	Polyurethane nanocomposite and yttrium aluminium garnet doped with terbium (III).	Luminescence

Analyzing table 3, one can see that the predominant property is luminescence, accounting for 40% of the investigated works with yttrium. Next is the flame retardant property, which yttrium citrate was used to obtain thermal stability in the 20% work range. After that, with about 20% of the works there are the composite with zirconia nanoparticles, which presents insulating properties. Finally, with 20% of the investigated works yttrium was used as a complement in the polyaniline and PU nanocomposite to obtain electromagnetic properties (Albayrak *et al.*, 2012; X. Chen *et al.*, 2021; Ryszkowska *et al.*, 2007; Saidi & Kadkhodayan, 2021; Yao *et al.*, 2021).

When evaluating the applications of PU with yttrium, the largest occurrence is concentrated in the electromagnetic area, in which nanocomposites with yttrium are widely used. The PU elastomer stands out by presenting surface protection, which regenerates through luminescent responses. Finally, the yttrium-doped zirconia nanocomposite has applications in electrical insulation, since the addition of inorganic additives at the nanoscale influences the insulating properties of the material, with a consequent improvement (Albayrak *et al.*, 2012; Ryszkowska *et al.*, 2007; Saidi & Kadkhodayan, 2021; Yao *et al.*, 2021).

3.2. Polyurethanes with La

Table 4 - Selected works involving polyurethane with lanthanum.

Work	Final material	Property
(Y. Pan et al., 2020)	Lanthanum phenylphosphonate film.	Flame Retardancy
(Saidi & Kadkhodayan, 2021)	Polyanilide/polyurethane nanocomposite with yttrium nitrate and $La_{1.8}Sr_{0.2}Ni_{1-x}Co_xO_4$-$CaCu_3Ti_{4-x}Nb_xO_{12}$ $(0 < x < 1)$.	Electromagnetic

(Z. Yin et al., 2021)	Composite of flexible polyurethane foam, ammonium polyphosphate and lanthanum tinate.	Flame Retardancy
(Qian et al., 2020)	Dual layered hydroxide composite with graphene oxide, thermoplastic polyurethane with lanthanum and hydroxide/graphene oxide hybrid.	Flame Retardancy
(Salazar-Muñoz et al., 2021, p.)	Polyurethane composite with manganite particles and $La_{0.67}Ca_{0.28}Sr_{0.05}MnO_3$.	Electromagnetic
(Xiao et al., 2017)	Hyper-fluorinated polyurethane and lanthanum(III) oxide composite.	Hydrophobicity
(Gbur et al., 2013)	Lanthanum doped zinc oxide polyurethane nanocomposite.	Luminescence
(Z. Liu et al., 2004)	Lanthanum chloride polyurethane composite.	None
(X. Shen et al., 2011)	Manganite with polyurethane and $La_{0.8}Sr_{0.2}MnO_3$	Optical properties
(Lu et al., 2013)	Lanthanum chloride polyurethane film.	Biocompatibility
(R. Yu et al., 2017)	Electrolyte composite with polyurethane and $Li_7La_3Zr_2O_{12}$.	Ionic conductivity
(Macaskie et al., 2005)	Biofilm of hydroxyapatite, polyurethane, titanium metal and lanthanum phosphate.	Biocompatibility
(Chi et al., 2018)	Lanthanum chloride polyurethane film with poly(2-methacryloyloxyethyl phosphorylcholine).	Biocompatibility

According to table 4, it is possible to observe that the property that appears most among the materials is that of flame retardancy, with approximately 23% of the 13 analyzed works. Next in the electromagnetic area there are properties of electromagnetic wave absorption, infrared emission and luminescence accounting for about 23%. Subsequently, in the biomedical field one finds properties such as platelet adhesion and also application as bone implants totaling close to 23% among the investigated works (Chi *et al*., 2018; Lu *et al*., 2013; Y. Pan *et al*., 2020; Qian *et al*., 2020; Saidi & Kadkhodayan, 2021; X. Shen *et al*., 2011; Z. Yin *et al*., 2021).

The remaining of analyzed works involving composites and films presented distinct properties, adding up to about 30% of these works. Among the less recurrent properties, there is the magnetocaloric property, which is a reversible magneto-thermodynamic phenomenon, which occurs due to the variation of a magnetic field. In addition, only one work among all the analyzed papers did not present any property, it was the composite of lanthanum chloride with PU (Gbur *et al*., 2013; Z. Liu *et al*., 2004; Macaskie *et al*., 2005; Salazar-Muñoz *et al*., 2021; Xiao *et al*., 2017; R. Yu *et al*., 2017).

Analyzing the applications with PU and lanthanum materials, it is observed that the largest application of these materials is concentrated in the biomedical area, with the use of biofilms and films for platelet adhesion and compatibility with bone tissue. PU substrate films were found to have excellent blood compatibility, due to the protein uptake that occurs immediately after platelet adhesion. For compatibility with bone tissue, hydroxyapatite was used, since its chemical nature is very similar to human bone, but it has unsatisfactory mechanical properties. Due to this fact, the addition of other materials such as PU is necessary. Sequentially, involving absorption and emission of electromagnetic waves, there are PU nanocomposites, which present characteristics of absorption and luminescence, besides the material with manganite and PU whose property is infrared emission, which presented potential applications in constructions (Chi *et al*., 2018; Gbur *et al*., 2013; Lu *et al*., 2013; Macaskie *et al*., 2005; Saidi & Kadkhodayan, 2021; X. Shen *et al*., 2011).

Despite a considerable amount of work involving composites and films with flame retardant properties, only one presented an application: the composite of ammonium polyphosphate with flexible PU foam and lanthanum in the field of civil construction (Y. Pan *et al*., 2020; Qian *et al*., 2020; Z. Yin *et al*., 2021).

Among the various applications concerning composites, there is the hyper-fluorinated PU, which presents hydrophobic characteristics and with applicability as an anti-fouling material. And finally, thermoplastic PU with electrolyte whose property is ionic conductivity has the applicability in solid state batteries (Xiao *et al*., 2017; R. Yu *et al*., 2017).

3.3. Polyurethanes with Ce

Table 5 - Selected works involving polyurethane with cerium.

Work	Final material	Property
(Jaganathan et al., 2022)	Polyurethane, beetroot and cerium(IV) oxide composite.	Hydrophobicity, biocompatibility and mechanics
(Mani et al., 2022)	Polyurethane and cerium(IV) oxide composite.	Hydrophobicity, biocompatibility and mechanics
(Ni et al., 2021)	Waterborne polyurethane, palygorskite and Ce^{3+} composite.	Corrosion resistance
(Huang et al., 2022)	Polyurethane and cerium(IV) oxide composite.	Corrosion resistance, radiation and mechanical resistance
(Xie et al., 2021)	Polyurethane and cerium(IV) oxide elastomer.	Mechanical
(Joshi et al., 2022)	Polyurethane and cerium(IV) oxide composite.	UV radiation resistance, corrosion resistance and thermal resistance
(Unnithan et al., 2014)	Polyurethane, biopolymer and cerium(IV) oxide composite.	Bactericide
(Mastouri Mansourabad et al., 2020)	Polyurethane, silicon oxide and cerium(IV) oxide composite.	Mechanical
(Nhiem et al., 2018)	Polyurethane and cerium(IV) oxide composite.	UV radiation resistance
(Baig & Khan, 2015)	Polyurethane and cerium(IV) phosphate composite.	Cu(II) sensorality
(Nguyen et al., 2021)	Polyurethane, silicon oxide and cerium(IV) oxide composite.	UV radiation resistance
(G.-F. Pan et al., 2022)	Polyurethane, cerium(III) trifluoromethanesulfonate and phloretin composite.	Mechanical
(X. Yu et al., 2021)	Polyurethane, polyacrylate and cerium(IV) oxide composite.	UV radiation resistance, thermal

		resistance and corrosion resistance
(S. Wang et al., 2019)	Thermoplastic polyurethane, cerium(IV) oxide and graphene oxide composite.	Flame retardancy
(Mo et al., 2019)	Waterborne polyurethane, Ce^{3+} and montmorillonite composite.	Corrosion resistance
(X. Yu et al., 2022)	Flexible polyurethane, cerium stannate and graphene composite.	Flame retardancy
(Ferrel-Álvarez et al., 2017, p.)	Waterborne polyurethane and cerium(IV) oxide composite.	UV radiation resistance
(Jorcin et al., 2010)	Shape memory polyurethane and Ce^{3+} composite.	Mechanical
(Anand & Sivaramakrishna, 2021)	Polyurethane, phosphine oxides and cerium(IV) oxide composite.	Catalytic activity
(Samardžija et al., 2022)	Polyurethane and Ce^{3+}, Ti^{2+} and Ni^{2+} phosphates.	Corrosion resistance
(A. Saadat-Monfared & Mohseni, 2014)	Polyurethane and cerium(IV) oxide nanoparticles composite.	UV radiation resistance
(Saadat-Monfared et al., 2012)	Polyurethane and cerium(IV) oxide nanoparticles composite.	UV radiation resistance
(Saha et al., 2019)	Polyurethane and cerium(IV) oxide nanoparticles composite.	Sensitivity to H_2O_2
(Xavier, 2021)	Polyurethane, polydopamine and cerium(IV) oxide nanoparticles composite.	Corrosion resistance
(Roitti et al., 2004)	Polyurethane and ceria-stabilized zirconia composite.	Catalytic activity
(Bose et al., 2022)	Polyurethane and cerium(IV) oxide nanoparticles composite	Mechanical
(Fu et al., 2016)	Polyurethane and cerium(IV) oxide nanoparticles composite.	Thermal resistance
(Palma-Ramírez et al., 2017)	Polyurethane, poly(methyl methacrylate) and cerium(III) phosphate nanoparticles composite	Luminescence and Mechanical
(Martineau & Shek, 2006)	Polyurethane, hydrogel and cerium(III) nitrate composite	None

As illustrated by figure 1, it was identified that studies containing PU and cerium were the most commonly found in the present research, in 32% of the papers, which are described in table 5. For the production of these materials, the most frequent cerium precursors are cerium(III) nitrate and cerium(IV) oxide. For the second case, both macroscopic and nanostructured precursors were found. For the polymeric matrix, it was found that approximately 50% of the works acquire the PU commercially, while the others usually synthesize it through the reaction of various polyols with different types of isocyanates.

Regarding the final material, it was possible to identify a tendency to use cerium(IV) oxide, whether nanostructured or not, in PU matrix, causing changes in its physical-chemical properties. In some papers, there were more complex combinations in which PU and cerium were found together with other chemical species.

The physicochemical property of greatest interest in the analyzed studies was the ability to resist the incidence of ultraviolet radiation that cerium can provide to the composites in which it is inserted, which is possible due to UV absorption with the generation of fewer free radicals and without much photoactivity (Saadat-Monfared *et al.*, 2012). This was evidenced in the work of

Saadat-Monfared *et al*. (2012), Saadat-Monfared and Mohseni (2014), Ferrel-Álvarez *et al*. (2017), Nhiem *et al*. (2018), Nguyen *et al*. (2021), X. Yu *et al*. (2021), Huang *et al*. (2022) and Joshi *et al*. (2022).

Mechanical properties were also improved by adding cerium to the materials, which was studied by Jaganathan and Mani *et al*. (2021), Xie *et al*. (2021), Huang *et al*. (2022), Jaganathan *et al*. (2022), Mani *et al*. (2022) and G.-F. Pan *et al*. (2022). The work reported by Jaganathan *et al*. (2022) used PU with cerium(IV) oxide and found that the addition of CeO_2 has made the material hydrophobic, as well as increasing blood clotting time and improving tensile strength, important characteristics for application in cardiac tissue engineering.

Mani *et al*. (2022) developed PU scaffolds with CeO_2 and found that with the addition of cerium the material presented hydrophobic nature. Moreover, the coagulation tests demonstrated a slow coagulation time, as well as good thermal and mechanical stability, essential properties for use in tissue engineering.

The main characteristic evaluated was the increase in tensile strength, which can occur when the size of the cerium(IV) oxide aggregates are compatible with the hard domains (HD) of the polymeric matrix, strengthening the cross-linking. Consequently, when the agglomerates present larger sizes at higher cerium concentrations in the composites, the mechanical properties are reduced (Xie *et al*., 2021).

Among the other physicochemical properties of interest that were analyzed in the articles categorized here, thermal resistance also stands out, studied by Xie *et al*. (2021), X. Yu *et al*. (2021), Mani *et al*. (2022) and Joshi *et al*. (2022), and corrosion resistance, verified by Mo *et al*. (2019), Ni *et al*. (2021), Samardžija *et al* (2022) and Huang *et al*. (2022). Hardness, hydrophobicity and anticoagulant capacity were identified in some papers, while other miscellaneous characteristics had lesser occurrence, such as regeneration capacity, resistance to water absorption and abrasion, anti-freeze property and flame retardants.

In the study of Unnithan *et al*. (2014), a material that combined PU, cellulose acetate, Zein and cerium(IV) oxide in the form of nanofibers demonstrated bactericidal capacity for several species, such as *Escherichia coli*, *Klebsiella pneumoniae*, *Salmonella enterica*, *Staphylococcus aureus* and *Enterococcus faecalis*. The authors identified that the concentration of the composite nanofibers influence the inhibition of Gram-positive and Gram-negative bacteria, and the mechanism of action involves damage to the cell membrane of microorganisms due to the ions Ce^{4+} released by the material.

Catalytic properties were also identified in the aforementioned papers. In one of the cases, Roitti *et al*. (2004) noted that the combination of PU with ceria-stabilized tetragonal zirconia produced a material capable of acting in the oxireduction of other reactions, according to the Temperature Programmed Reduction, process that takes place on the surface of the composite. In another case, Anand and Sivaramakrishna (2021) studied the catalytic property of polyurethane, phosphine oxides and cerium(IV) oxide composite ahead of obtaining derivatives of biscoumarin. The results were positive and presented reusability, reaching up to ten reaction cycles with yields around 90% in just two hours of reaction at 80 ºC.

Baig and Khan (2015) have verified the use of a cerium(IV) phosphate PU composite with a cation exchange permeable membrane. Potentiometric measurements indicated that the material was able to detect and measure ions Cu^{2+} at different concentrations, and that the electrodes had good reproducibility and homogeneity in their detection property. The detection of other substances has also been identified in the cerium work, such as Saha *et al*. (2019). The researchers used a PU scaffold embedded with cerium(IV) oxide nanoparticles to detect hydrogen peroxide. The tests revealed that the material was sensitive at low concentrations, reaching 3.18 μM as a limit of H_2O_2. Furthermore, the responses were quick and there was the possibility of reusing the material.

Pan *et al*. (2022) noted that the polyurethane composite, cerium(III) trifluoromethanesulfonate and phloretin forms coordination bonds between hydroxyl groups of the phloretin and the isocyanate groups of polyurethane prepolymer, allowing the final elastomer to have renegerative capabilities. After being cut and placed in a mold, a period of 48 hours was sufficient for the material to resume its original mechanical properties, being able to revert to the initial tensile strength. In addition, the thermoplasticity of the composite allows it to be recycled more easily.

In the study of Fu *et al*. (2016), antifreeze properties of polyurethane and cerium(IV) oxide nanoparticles were verified. This was possible due to the hydrophobicity presented by the material under certain surface conditions. According to the authors, morphology and surface energy affect the interaction with water and ice, which was verified by wettability measurements and electron microscopy. More hydrophobic surfaces lead to the formation of more spherically shaped ice, which makes it easier to remove compared to ice formed flat.

3.4. Polyurethanes with Nd

Table 6 - Selected works involving polyurethane with neodymium.

Work	Final material	Property
(Mendes-Felipe et al., 2021)	Acrylated polyurethane nanocomposite, iron(III,IV) oxide, cobalt ferrite and neodymium iron boron alloy	Eletromagnetic
(Yao et al., 2021)	Polyurethane elastomer with carbon dots and neodymium chloride	Luminescence
(R.-C. Liu et al., 2019)	Thermoplastic polyurethane nanocomposite with neodymium(III) oxide	Thermal resistance

Observing table 6, it is possible to notice a heterogeneity in relation to the investigated properties, such as luminescence, thermal and magnetic resistance (R.-C. Liu *et al*., 2019; Mendes-Felipe *et al*., 2021; Yao *et al*., 2021).

Regarding the applications of the analyzed works, the neodymium-containing PU elastomer shows a self-healing application responsive to fluorescence thanks to the lanthanide in its structure. As for the neodymium nanocomposite, its magnetic property allows specific applications involving magneto-responsive structures. Finally, the nanocomposite of thermoplastic PU and neodymium did not show any application (R.-C. Liu *et al*., 2019; Mendes-Felipe *et al*., 2021; Yao *et al*., 2021).

3.5. Polyurethanes with Eu

Table 7 - Selected works involving polyurethane with europium.

Work	Final material	Porperty
(Fiedler et al., 2007)	Polyurethane and europium p-aminobenzoate complex composite	Luminescence and UV radiation resistance
(Qian et al., 2021)	Thermoplastic polyurethane, zinc borate, graphene oxide composite with Eu, Mg and Al	Flame retardancy
(Li et al., 2020)	Polyurethane elastomer and Eu composite	Luminescence
(X. Wang et al., 2012)	Waterborne polyurethane and europium 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)1,3-propanedione nanoparticles composite	UV radiation resistance and thermal resistance
(Jiang et al., 2013)	Polyurethane, silicon oxide and europium benzoic acid and 1,10-phenanthroline complex composite	Luminescence

(Beltyukova & Balamtsarashvili, 1995)	Europium thenoyltrifluoroacetone and 1,10-phenanthroline complex sorbed in polyurethane	Luminescence
(Z. Zhou et al., 2013)	Polyurethane, silicon oxide and europium composite	Luminescence
(S. Zhou et al., 2007)	Polyurethane and europium methacrylic acid complex composite	Luminescence
(Reisfeld et al., 2003)	Polyurethane, silicon oxide, zirconium, europium cryptate, europium sulfide and europium oxide composites	Luminescence
(Ma et al., 2021)	Poly(siloxane-urethane) and europium elastomer	Luminescence
(L. Gao et al., 2019)	Polyurethane and europium p-hydroxybenzoic acid complex composite	Luminescence
(Basu & Vasantharajan, 2008)	Polyurethane and europium thenoyltrifluoroacetonate composite	Luminescence
(Saeed et al., 2005)	Polyurethane and 1-(2-pyridylazo)-2-naphthol composite with sorbed Eu^{3+}	None
(Ilmi et al., 2019)	Polyurethane and europium thenoyltrifluoroacetonate 2,2—dipyridylamine complex composite	UV radiation resistance, thermal and mechanical resistance
(Su, Zhang, Jia, Gao, Li, He, et al., 2019)	Polyurethane and europium thenoyltrifluoroacetonate 1,10-phenanthroline complex composite	Luminescence, Cu(II) sensitivity
(W. Zhang et al., 2022)	Polyurethane, sulfur quantum dots and europium 2,2—dipyridylamine complex composite	Luminescence and mechanical
(Xu et al., 2018)	Polyurethane and europium thenoyltrifluoroacetonate 1,10-phenanthroline complex composite	Luminescence
(Garcia-Torres et al., 2014)	Polyurethane and europium thenoyltrifluoroacetonate 1,10-phenanthroline complex composite	Luminescence
(Reisfeld et al., 2009)	Polyurethane, silicon oxide, silver nanoparticles and europium complexes composites	Luminescence
(Reisfeld, 2004)	Polyurethane, zirconia and europium sulfide composite	Luminescence

Materials containing europium and PU were identified in 23% of the reviewed papers. For its production, a similar trend was observed to the studies involving cerium. Some authors synthesize their own PU from various polyols and isocyanates, while others purchase the product commercially. As europium precursors, europium chloride and europium oxide were found to be the most commonly used, followed by europium nitrate. However, one difference with cerium is the appearance of europium complexes, such as europium thenoyltrifluoroacetonate complex or europium p-hydroxybenzoic acid complex, in the final structure of the composites produced.

Through table 7, it was possible to notice that the most explored physicochemical property of the PU and europium composites was luminescence, present in almost all the analyzed papers. Rare earth metals, especially europium, are able to react to external stimuli and provide electronic transitions in the f sublevel, conferring luminescent property to the composite in which it is inserted (Li *et al*., 2020).

In one of the papers, Su *et al*. (2019) found that the luminescence of the PU composite with europium complexes ceases with the addition of ions Cu^{2+}, enabling the material to act as a detector of these ions in aqueous solutions at low concentrations such as 0.28 μM, while other ions did not cause such a change. Furthermore, the luminescence can be reused after washing, while the addition of 1,10-phenanthroline complex has further increased the reusability of the detector.

Although luminescence has also been studied, the work of W. Zhang *et al*. (2022) identified the regenerative property in the composite of polyurethane, sulfur quantum dots and europium 2,2-dipyridylamine complex. The regeneration process usually takes place through the use of dynamic bonds capable of restoring themselves. The final material has shown good mechanical properties, being elongated up to eight times without breaking and being able to support up to 2700 times its own weight. Regeneration tests have shown that the mechanical properties remain virtually unchanged, even after the material is intentionally cut.

3.6. Polyurethanes with Gd

Table 8 - Selected works involving polyurethane with gadolinium.

Work	Final material	Property
(Fiedler et al., 2007)	Polyurethane composite and terbium *p*-aminobenzoates	Luminescence
(Cai et al., 2020)	Polyurethane composite with hexagonal phase sodium gadolinium fluoride doped with ytterbium Polyurethane composite with hexagonal phase sodium gadolinium fluoride doped with thulium	Luminescence
(X. Gao et al., 2022)	Polyurethane nanocomposite and gadolinium-diethylenetriamine pentaacetate and folic acid.	Luminescence

According to table 8, the prevalent property is luminescence, totaling about 66% among the investigated gadolinium works. The other remaining work has the contrast agent property (Cai *et al*., 2020; Fiedler *et al*., 2007; X. Gao *et al*., 2022).

By examining the applications between PU and gadolinium, it is noted that all composites that presented luminescence property were applied in optical systems, such as in devices and detectors. On the other hand, the nanocomposite with contrast agent property was used for tumor diagnosis because of the high fluorescence of gadolinium (Cai *et al*., 2020; Fiedler *et al*., 2007; X. Gao *et al*., 2022).

3.7. Polyurethanes with Tb

Table 9 - Selected works involving polyurethane with terbium.

Work	Final material	Property
(Fiedler et al., 2007)	Polyurethane composite and terbium *p*-aminobenzoates	Luminescence
(Ryszkowska et al., 2007)	Polyurethane nanocomposite and yttrium aluminum garnet doped with terbium(III)	Luminescence
(Reisfeld et al., 2003)	Zirconium-silica-polyurethane films with terbium sulfide	Luminescence

	Zirconium-silica-polyurethane films with terbium tri-(diphenylphosphorilamine)	
(W. Zhang et al., 2022)	Polyuretane crosslink and polyethylene glycol with sulfur quantum dots with $Na_3[Tb(dpa)_3]$	Luminescence
(Reisfeld, 2004)	Polyurethane composite and terbium sulfide and polyurethane composite with terbium oxide	Luminescence
(Xi et al., 2017)	Polyurethane composite with polymethyl methacrylate functionalized with terbium(III)	Luminescence
(Hilder et al., 2008)	Polyrethane composite with terbium carboxylate Polyurethane composite with terbium diethyleneglycolhexafluoroacetylacetonate	Optical properties
(Rong et al., 2020)	Polyurethane composite and functionalized silica with terbium(III)	Dopamine sensitivity
(J. Wang et al., 2013)	Polyurethane composite and functionalized silica with terbium(III)	Luminescence
(Su, Zhang, Jia, Gao, Li, Bai, et al., 2019)	Polyurethane with terbium anthranilinate	$H_2PO_4^-$ sensitivity
(Sun et al., 2010)	Polyurethane with terbium-tris[(2-hydroxy-benzoyl)-2-aminoethyl]amine	Luminescence
(Yang et al., 2022)	Polyurethane composite with $[Tb(PABA)_3Phen]$. (PABA = P-aminobenzoic acid)	Luminescence and UV radiation resistance
(Villagra et al., 2021)	Polyurethane with terbium nitrate and polyurethane with $[TbL\ (NO_3)_2](NO_3)(H_2O)$, being (L = N6 macrocyclic ligand)	Luminescence
(Suenaga et al., 2008)	Polyurethane coated with $Fe_{3.2}Tb$	Electromagnetic

According to table 9, one notes the predominance of the study of the luminescent properties of terbium (Fiedler *et al*., 2007; Reisfeld, 2004; Reisfeld *et al*., 2003; Ryszkowska *et al*., 2007; Sun *et al*., 2010; Villagra *et al*., 2021; J. Wang *et al*., 2013; Xi *et al*., 2017; W. Zhang *et al*., 2022), all the articles state that luminescence is a potential characteristic of terbium compounds for photochemical and photophysical applications. The work of Reisfeld (2004) does not report the precursors, it is because the paper was written by Renata Reisfeld in memory of the professor Christian K. Jørgensen, not detailing how the materials discussed in the work were obtained.

Hilder *et al*. (2008) and Yang *et al*. (2022) although not focusing on the luminescence of terbium compounds, have also studied the optical properties. The report of obtaining the transparent composite by Hilder *et al*. (2008) becomes interesting because it indicates the possibility of obtaining these types of materials. Yang *et al*. (2022) have contributed to the study of the application of lanthanides as an additive for resistance to degradation by UV radiation, which is attributed to the fluorescence property that terbium compounds possess. Suenaga *et al*. (2008) coated PU with an iron-terbium alloy, analyzing how the material deforms when subjected to a magnetic field. The authors concluded that the sample has a high susceptibility to deformation due to the inherent flexibility of PU.

Rong *et al*. (2020) and Su *et al*. (2019) develop materials that have the ability to act as sensors due to the Tb(III) ion in their structure. Rong *et al*. (2020) synthesized a material that is sensitive to the dopamine molecule in aqueous solution, showing that the material has selectivity and can be used for the fast and effective detection of dopamine. The authors point out that this type of material may in the future be used in laboratory equipment and produced based on 3D printing. Su *et al.* (2019) have developed a material that can detect the ion $H_2PO_4^-$, very recurrent in biological systems and one of the chemical species used for determining the purity of water. The authors state that the material is sensitive and highly selective, and that the chromophore used (with terbium in its structure) binds by covalent bonding to the PU structure, making the material stable and can be used several times.

3.8. Polyurethanes with Er

Table 10 - Selected works involving polyurethane with erbium.

Work	Final material	Property
(Yao et al., 2021)	Polyurethane elastomer with carbon dots and erbium chloride	Luminescence

As shown in table 10, there is only one PU elastomer paper that used the erbium lanthanide, which contains the fluorescence property. Besides the material presenting application for healing scratches on its surface, because it is a functional material, it also obtained high hardness (Yao *et al.*, 2021).

3.9. Polyurethanes with Tm

Table 11 - Selected works involving polyurethane with thulium.

Work	Final material	Property
(Cai et al., 2020)	Polyurethane composite with hexagonal phase sodium gadolinium fluoride doped with thulium	Luminescence

According to table 11, only one work was found on a PU composite, which used thulium, which presents luminescent properties. Regarding the applications of this lanthanide, its optical applications stand out, which can be applied in photovoltaic systems and optical memories (Cai *et al.*, 2020).

3.10. Polyurethanes with Yb

Table 12 - Selected works involving polyurethane with ytterbium.

Work	Final material	Property
(Yao et al., 2021)	Polyurethane elastomer with carbon dots and ytterbium chloride	Luminescence
(Cai et al., 2020)	Polyurethane composite with hexagonal phase sodium gadolinium fluoride doped with ytterbium	Luminescence

According to table 12, among the two investigated works, the common property found is luminescence. As for the application, the elastomer of PU and terbium can be applied in the area of protective coatings, which can be used for flexible screens. The composite containing ytterbium has its application focused on nanodevices with luminescence properties such as lasers (Cai *et al.*, 2020; Yao *et al.*, 2021).

3.11. Polyurethanes with Lu

Table 13 - Selected works involving polyurethane with lutetium.

Work	Final material	Property
(Zugle et al., 2011)	Polyurethane composite with 2(3), 9(10), 16(17), 23(24)-(tetracarboxyphenoxyphthalocyaninato) lutetium(III) acetate	Electromagetic

Observing table 13, it was found only one work of PU composite that used lutetium, which presents diamagnetic property. This material can be used in photocatalytic reactions, with the possibility of application for degradation of pollutants (Zugle *et al*., 2011).

4. Conclusions

Based on the study presented here, it was possible to identify a wide range of papers listed on the Web of Science platform involving materials containing PU and rare earth elements, although not all of these were represented. The analysis indicated that cerium, europium, terbium and lanthanum are the rare earth chemical elements most often combined with PU matrices, probably as a result of their greater abundance and the interest in their physicochemical properties, which can enhance the final material.

In a smaller proportion, articles involving PU with yttrium, neodymium, gadolinium, erbium, thulium, ytterbium and lutetium were also categorized. No papers combining PU with scandium, praseodymium, promethium, samarium, dysprosium and holmium were found, indicating that the research line still has potential for consolidation of new materials.

It was found that the physicochemical property of greatest interest in the combination of PU with rare earth elements was luminescence, with most of the papers for each chemical element analyzed focusing on such property, with the exception of lanthanum, cerium and lutetium, which respectively presented characteristics of flame retardancy, resistance to ultraviolet light and diamagnetism.

Overall, the analysis has shown that the rare earth chemical elements can be inserted into PU matrices and their characteristics used in the resulting material for different applications. Often, more complex combinations have been made, inserting other metals, complexes, oxides, polymers and even bioactive molecules, allowing the application of new composites as coatings, anticoagulants, resistant polymer resins in the area of tissue engineering and regeneration and even as bactericides.

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