



Polyaniline: Trends and perspectives from text mining analysis

Fernando Gomes de Souza Jr^{1,2}

1. Instituto de Macromoléculas Professora Eloisa Mano, Centro de Tecnologia-Cidade Universitária, av. Horacio Macedo, 2030, bloco J. Universidade Federal do Rio de Janeiro, Brazil, ZIP Code 21941-598

2. Programa de Engenharia da Nanotecnologia, COPPE, Centro de Tecnologia-Cidade Universitária, av. Horacio Macedo, 2030, bloco I. Universidade Federal do Rio de Janeiro, Brazil, ZIP Code 21941-972 - fgsj@ufrj.br

Abstract: Polyaniline (PAni) is the oldest and most studied conductive polymer in the world. This polymer, reported by Letheby in 1862, was substantially better understood due to the tireless efforts of hundreds of scientists. Among them, Professor Alan G. MacDiarmid has contributed with more than one hundred and twenty published papers about PAni. During his last visit to Brazil (MACRO / IUPAC-2006), Professor MacDiarmid stated that "... I am sure there is still much to be studied about polyaniline...". Thus, the objective of this work is to carry out a Text Mining on PAni in the two last decades. For that, the main keywords associated with the material in question will be presented, year by year. This approach allowed seeing how the theme has evolved during this period. Besides that, Text Mining has helped us to extrapolate scenarios for the coming years. Thus, Nanotechnology, Molecular Modeling, and polyaniline will be the main drivers for accelerating the arrival of a new world, where science, machines, systems, and people will work together, bringing more efficient results and increasingly strategic processes, which will benefit all Humankind.

Keywords: Data analysis, Statistical analysis, Data mining, Polyaniline, synthesis, super-capacitor, sensor, properties, preparation, performance, oxide, nanoparticles, nanofibers, nanocomposite, modified, high, graphene, films, enhanced, electrode, electrochemical, doped, conducting, composite, characterization, carbon, application, acid.

Adherence to the BJEDIS' scope: This work is closely related to the scope of BJEDIS as it presents a text mining that allows foreseeing trends on polyaniline applications.

*Address correspondence to this author at the Biopolymers & Sensors Lab. / Macromolecules Institute / Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil; Tel/Fax: +55-21-3938-7766; E-mails fgsj@ufrj.br



1. INTRODUCTION

Polymers are usually associated with electrical insulators (1, 2). This association is, undoubtedly, closely related to the many initial applications of these materials in the electrical and electronic areas, where they have been and continue to be used extensively as replacements for insulators made of paper (3, 4).

In the last century, during the '70s, iodine-doped poly-acetylene emerged from Shirakawa's research (5). This material had an intrinsically electroactive behavior, in addition to the electrical conductivity of the same order of magnitude as some metals at room temperature. These materials were then called "synthetic metals" (6) or "intrinsic conducting polymers" (7), ICP, and have been studied with great interest ever since (8–10).

Among the intrinsic conducting polymers, Polyaniline (PAni) is a conducting polymer (11–37), resulting from the oxidative polymerization of aniline (38–56). PAni's conductivity can be affected by the degree of doping, the type of dopant (57), the morphology (58), and the degree of crystallization (59). Polyaniline was firstly reported by Letheby (60) in 1862 .

Polyanilines represent a class of polymers whose chemical composition in base form, that is, in dedoped form, is given by a general formula presented in Figure 1. This general formula is composed of "y" and "1 - y" repetitive units of the reduced and oxidized species, respectively (61). The value of "y" can vary continuously from 1, for the wholly reduced polymer (which contains only nitrogen amine groups), to zero, for the entirely oxidized polymer (which contains only nitrogen imine groups). The following terms designate the different oxidation degrees of the PAni: leucoemeraldine, protoemeraldine, emeraldine, nigraniline, and pernigraniline. These oxidation states present "y" equal to 1; 0.75; 0.5; 0.25; and 0, respectively (62).

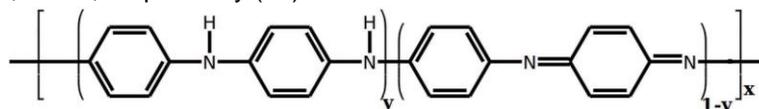


Figure 1 - General formula of polyaniline in the non-protonated form.

PAni has attracted much attention in recent decades due to its characteristics such as low cost, high conductivity, and excellent resistance to the environment. Besides that, PAni presents unique electronic properties. These properties can be reversibly controlled by the protonation/deprotonation processes (63). Besides, PAni possesses an excellent potential for cutting-edge applications (64). Among these applications, electrodes (65, 66), batteries (67, 68), microelectronics (69, 70), displays (71), electromagnetic shielding (72), and sensors (73, 74) deserve to be highlighted.

Polymers are vital materials for the Humankind and have been widely researched by Biopolymers and Sensors Lab Group from Universidade Federal do Rio de Janeiro (35, 75–187). Over the past few years, we have contributed to the polyaniline field by producing new materials. These materials were used as pressure (35, 76, 99, 124, 145, 160) , gas (78, 114) and magnetic (130) sensors. Over the years, we realized the need to improve the preparation of these materials, making them more Eco-friendly than the ordinary blends. Thus, we choose for the modification of vegetable substrates with thin layers of polyaniline, preserving the macro properties of the substrates and generating, from the coatings, new chemical-electrical properties. This new route allowed the preparation of further pressure, temperature, and even acid vapors sensors (89, 97, 101, 138, 141). These contributions drove our interest in understanding the evolution of the theme over the past two decades. For that, we used Text Mining tools that were very valuable to identify the main contributions to this theme, allowing us to draw a picture year by year based on correlation analyzes. So, this work aims to describe the development of the theme polyaniline over the 2009-2019 decades. For this, the leading publications of each year were collected. These works were then studied using online text analysis tools. These tools, widely available, made it possible to draw a detailed overview of the

main discussions about polyaniline, showing the evolution of the theme. Besides, the retrieved information allows us to foresee the perspectives referring to polyaniline in the near future.

2. Methodology

Scientific articles containing the word polyaniline in the title were collected using the ScienceDirect database. More specifically, 3041 scientific articles were collected between 1999 and 2019. Of course, these numbers can vary depending on the used database. These articles were separated into the following topics: (i) title, (ii) abstract, and (iii) journal. This procedure allowed analyzing the main words listed in the documents, besides determining which Journals contributed profoundly to the dissemination of the studies about polyaniline. The used tools were LibreOffice Calc and LibreOffice Writer (both version: 6.2.8.2 Build ID: 1:6.2.8-0ubuntu0.19.04.1). The online tools Textalyser (<http://textalyser.net/>), Wordcloud (<https://www.jasondavies.com/wordcloud/>), and Voyant tools (188, 189) (<https://voyant-tools.org/>) were used to the Text Mining of the most relevant words in the texts. The conditions used in the Wordcloud website tool were: Spiral - Archimedean; Scale - n; 5 orientations from -60° to 60°; and number of words - 250. In turn, the conditions used in the Textalyser website tool were: Minimum characters per word - 3; special word or expression to analyze - None; number of words to be analyzed - 30; ignore numbers - On. Finally, the set conditions in the Voyant tolls were Fixed term - polyaniline and minimum coverage - 5%.

3. Results

Text Mining is a variation in data mining (190–193), which allows data extraction from text documents (194–197). Also, Text Mining has immeasurable commercial value and can be a handy tool in areas as diverse as medicine and customer service (198–200). As could not have been otherwise, the general scenario between the years 1999 and 2019 is complex and quite challenging to understand because of the gigantic papers collected. For example, among the 3041 scientific documents, 38233 and 476258 words were counted in the titles and abstracts, respectively.

Therefore, the analysis of this scenario requires computational assistance that can be offered by Text Mining tools. Then, the first approach was performed using the Wordcloud tool . The results are shown in Figure 2.

Table 1 - Frequency and top words in 1999-2019 Titles & Abstracts

#	Titles				Abstracts			
	Word	Occurrences	Freq. (%)	Rank	Word	Occurrences	Freq. (%)	Rank
1	Polyaniline	2739	9.3	1	Polyaniline	4381	4.8	1
2	synthesis	385	1.3	2	high	564	0.6	2
3	composite	371	1.3	2	composite	558	0.6	2
4	based	366	1.2	3	electrochemical	495	0.5	3
5	properties	345	1.2	3	electrode	482	0.5	3
6	carbon	336	1.1	4	using	470	0.5	3
7	graphene	321	1.1	4	surface	439	0.5	3
8	electrochemical	307	1.0	5	conductivity	410	0.4	4
9	performance	306	1.0	5	performance	400	0.4	4
10	nanocomposite	235	0.8	6	properties	400	0.4	4
11	high	232	0.8	6	electron	399	0.4	4
12	composites	231	0.8	6	polymerization	396	0.4	4
13	characterization	227	0.8	6	prepared	393	0.4	4
14	oxide	223	0.8	6	carbon	365	0.4	4
15	doped	210	0.7	7	spectroscopy	347	0.4	4
16	electrode	187	0.6	8	based	329	0.4	4
17	films	186	0.6	8	structure	326	0.4	4
18	nanocomposites	184	0.6	8	method	322	0.4	4
19	preparation	175	0.6	8	aniline	316	0.3	5
20	using	159	0.5	9	results	307	0.3	5
21	super-capacitor	154	0.5	9	capacitance	300	0.3	5
22	acid	153	0.5	9	synthesized	296	0.3	5
23	nanofibers	151	0.5	9	acid	287	0.3	5
24	supercapacitors	147	0.5	9	nanocomposite	282	0.3	5
25	conducting	143	0.5	9	used	281	0.3	5
26	nanoparticles	140	0.5	9	showed	280	0.3	5
27	enhanced	139	0.5	9	film	279	0.3	5
28	modified	135	0.5	9	energy	277	0.3	5
29	application	134	0.5	9	specific	275	0.3	5
30	sensor	131	0.4	10	stability	264	0.3	5

Data extracted using <http://textalyser.net/index.php?lang=en#analysis>

By contrast, the two terms most negatively relevant are *polyaniline x carbon* and *polyaniline x oxide*. These negative values prove that these terms lost relevance along the studied period. In turn, the most irrelevant terms were *polyaniline x grafting* and *polyaniline x Co₃O₄*. A similar analysis can be performed to the Abstracts' contents, from which the most irrelevant terms are *polyaniline x ksc* (kenaf stem-derived macroporous carbon) and *polyaniline x ITO* (indium tin oxide). From this data set, the most relevant term is *polyaniline x nanofibers*. This result is due to the outstanding improvement of the conducting matrix properties by the insertion of nanofibers.

Table 2 - Correlations between polyaniline and 2nd terms in 1999-2019 Titles & Abstracts

Fixed term	Titles			Abstracts		
	2 nd term	Correlation	p	2 nd term	Correlation	p
Polyaniline	conducting*	0.9603	0.00001	nanofibers*	0.8640	0.00127
	films*	0.9364	0.00007	increased*	0.8478	0.00195
	acetate*	0.9111	0.00024	direct*	0.8210	0.00360
	grafting	0.0021	0.99549	ksc	0.0001	0.99986
	Co ₃ O ₄	-0.0007	0.99839	ITO	-0.0006	0.99871
	performance*	-0.8904	0.00055	CeO ₂ *	-0.8483	0.00192
	carbon*	-0.9186	0.00017	alkaline*	-0.8599	0.00142
	oxide*	-0.9216	0.00015	interpenetrating*	-0.8670	0.00116

* Statistically relevant terms

However, the more detailed observation on every year in the studied period is relevant to the understanding of the road-map that the subject polyaniline has followed along these twenty one years.

Aiming to perform this complex task, the Voyant's Correlation tool will be used again and the most relevant and irrelevant terms will be listed year by year. As done before, all PANi abbreviations were removed from the titles and abstracts.

Table 3 and 4 shown the correlations between polyaniline and the most relevant terms extracted, using Voyant Tools, from the Titles and Abstracts.

Again, terms that have statistical relevance ($p < 0.05$) were marked with asterisks. The highest correlation values, regardless of whether their sign is positive or negative, were listed in Tables 3 and 4. The most irrelevant term (with the highest p-value among the data set) was also listed. Besides, all of the generated Weblinks to Voyant Tools' corpus are listed in Table 5.

However, seeking to facilitate the understanding of the results obtained, in addition to reducing the length of the discussion, the analysis efforts will be concentrated on the positive correlation values. More specifically, the terms of the Title and Abstract that present the most significant correlations with the term polyaniline will be analyzed.

The purpose of this analysis is to present an instant regarding the subject in every year studied. This procedure points out the probable reason for this association between the disclosed themes.

Besides that, from every year's data collection, the most relevant work of that period and its number of citations, based on the ranking directly taken from ScienceDirect, will be presented.

Table 3 - Correlations between polyaniline and 2nd terms in 1999-2008 Titles & Abstracts

Fixed term	Titles			Abstracts			
	2 nd term	r	p	2 nd term	r	p	
Polyaniline	1999	electrical*	0.7295	0.01665	bands*	0.7961	0.00587
		glutaraldehyde	-0.0270	0.94107	particles	-1.9165	0.99999
		aluminum	-0.4673	0.17330	film*	-0.6817	0.02993
	2000	nanocomposite	0.2004	0.57872	host*	0.7028	0.02339
		electrochemical	-0.1336	0.71285	corrosion	0.0000	1.00000
		aniline	-0.4677	0.17285	parallel*	-0.7028	0.02339
	2001	conductivity*	0.7638	0.01013	enhanced*	0.7500	0.01248
		conducting	0.0476	0.89607	parent	0.0000	1.00000
		gas	-0.3273	0.35588	observed*	-0.7333	0.01580
	2002	conductive*	0.6667	0.03527	blends*	0.7824	0.00748
		corrosion	-0.1667	0.64538	base	0.0000	1.00000
		acid*	-0.7258	0.01749	higher*	-0.7487	0.01272
	2003	conducting*	0.6840	0.02917	metal*	0.7380	0.01481
		characterization*	-0.0468	0.89779	organic	0.0000	1.00000
		hybrid	-0.4588	0.18226	optical*	-0.7420	0.01401
	2004	based*	0.6296	0.05108	acrylamide	0.7740	0.00860
		composites	0.1455	0.68842	adsorption	-0.0079	0.98268
		mild	-0.4444	0.19813	higher*	-0.8235	0.00341
	2005	doped*	0.6667	0.03527	novel*	0.9056	0.00031
		chemical	-0.1021	0.77905	frequency	0.0000	0.99999
		poly	-0.5791	0.07941	base*	-0.7596	0.01081
	2006	dodecylhydrogensulfate*	0.8305	0.00293	oxidation*	0.9014	0.00037
		cobalt	0.0000	1.00000	deposited	0.0029	0.99304
		degradation*	-0.6343	0.04888	composites*	-0.6540	0.040239
	2007	hybrid*	0.7906	0.00648	parameters*	0.6856	0.02864
		coated	0.0000	1.00000	ferromagnetic	0.0000	0.99999
	conductivity*	-0.6901	0.02721	analyses*	-0.8081	0.00468	
2008	electrochemically*	0.6934	0.02618	disordered*	0.8424	0.00222	
	hydrogel	0.0605	0.86809	analysis	0.0007	0.99850	
	fiber*	-0.6934	0.02618	black*	-0.7435	0.01270	

* Statistically relevant terms

Table 4 - Correlations between polyaniline and 2nd terms in 2009-2019 Titles & Abstracts

Fixed term	Titles			Abstracts			
	2 nd term	r	p	2 nd term	r	p	
Polyaniline	2009	nanofibers*	0.6800	0.03051	phosphate*	0.8730	0.00097
		method	0.0507	0.88930	perfluorinated	0.0102	0.97770
		free*	-0.6935	0.02615	low*	-0.7500	0.01246
	2010	development*	0.8135	0.00420	NaCl*	0.9356	0.00007
		oxidase	0.0000	1.00000	indicated	0.0014	0.99704
		ions*	-0.6642	0.03619	lower*	-0.7831	0.00738
	2011	hydrogen*	0.8040	0.00506	carried*	0.7919	0.00633
		methanol	-0.0741	0.83885	exhibit	0.0000	1.00000
		applications	-0.5415	0.10596	capacity	-0.7958	0.00590
	2012	graphite*	0.7033	0.02325	deposited*	0.9741	0.00001
		copper	-0.0603	0.86853	convenient	0.0000	1.00000
		new*	-0.7293	0.01669	effective	-0.7589	0.01093
	2013	nanostructured*	0.8464	0.00202	exfoliation*	0.9295	0.00010
		battery	-0.0337	0.92638	indicating	0.0011	0.99755
		mesoporous*	-0.6690	0.03439	area	-0.8070	0.00477
	2014	electrode*	0.8462	0.00203	exposed*	0.9310	0.00009
		CO ₂	-0.0153	0.96656	electronic	-0.0006	0.99875
		phosphate*	-0.6493	0.04220	best*	-0.7884	0.00674
	2015	characterization*	0.8142	0.00414	monomer*	0.9345	0.00007
		doped	-0.0640	0.86053	ideally	0.0000	1.00000
		oxygen*	-0.7638	0.01013	area*	-0.7923	0.00628
	2016	acids*	0.9476	0.00003	chloroform*	0.8894	0.00057
		fabrication	-0.0439	0.90423	aspect	0.0000	0.99999
		corrosion*	-0.6964	0.02526	employed*	-0.8268	0.00317
	2017	anti-corrosion*	0.7633	0.01020	performed*	0.9161	0.00020
		degradation	-0.0353	0.92280	discharging	0.0000	1.00000
		electrical*	-0.7901	0.00654	exposed*	-0.7696	0.00923
2018	oxidation*	0.8359	0.00259	interaction*	0.8990	0.00040	
	hydrogen	0.1023	0.77862	contact	0.0000	0.99999	
	parameters	-0.2611	0.46624	fabricating*	-0.8507	0.00181	
2019	nanocomposites*	0.6715	0.03348	pd*	0.8530	0.00170	
	acetone	0.0448	0.90219	evaluate	0.0000	0.99999	
	healing*	-0.9366	0.00007	metal*	-0.8797	0.00079	

* Statistically relevant terms

Table 5 – Weblinks to Voyant Tools' corpus

Year	Titles
1999	https://voyant-tools.org/?corpus=da265905f6024c154c272a275080bcc6&lang=en
2000	https://voyant-tools.org/?corpus=ac72eda946720c4d223ccbe4d385927e&lang=en
2001	https://voyant-tools.org/?corpus=2f131ecc50ed85c09d4cc5d158351067&lang=en
2002	https://voyant-tools.org/?corpus=c9e9a743ae53d77759bf36bd9d6b9c8f&lang=en
2003	https://voyant-tools.org/?corpus=31813304e26f58516edc5f84dae8683a&lang=en
2004	https://voyant-tools.org/?corpus=6f1b99c617df0cd3df0a05e9a060b4b8&lang=en
2005	https://voyant-tools.org/?corpus=495ecb6ddd75fe9c6cf84c0630b4fc8d&lang=en
2006	https://voyant-tools.org/?corpus=b77a61cb13b2d2964955c91e0517eb87&lang=en
2007	https://voyant-tools.org/?corpus=9fec6090914210338e00114afd61ee46&lang=en
2008	https://voyant-tools.org/?corpus=a73522252d3d2228f157eca2f188fa8&lang=en
2009	https://voyant-tools.org/?corpus=f1eddb2872fa42e9df65b0dd573218c&lang=en
2010	https://voyant-tools.org/?corpus=633cc88748593e6c99e513b941d95f05&lang=en
2011	https://voyant-tools.org/?corpus=c4cf23cc3049a490fa47ac61e9a8a3c1&lang=en
2012	https://voyant-tools.org/?corpus=acd5c1465b7dd6f73bb51f54e88cd236&lang=en
2013	https://voyant-tools.org/?corpus=d6738232d08df8ed2dea96069d3dd7d7&lang=en
2014	https://voyant-tools.org/?corpus=c5880b355bf6c962379bc394862b8da4&lang=en
2015	https://voyant-tools.org/?corpus=f44a980a832e557825a32c6d1d59ada3&lang=en
2016	https://voyant-tools.org/?corpus=bf7e06843839169289e027919bbe3df8&lang=en
2017	https://voyant-tools.org/?corpus=bb4429cd73b4d4ac11c9f2abb18b0f7a&lang=en
2018	https://voyant-tools.org/?corpus=c441265a69730a6e4226b5924d04b4b4&lang=en
2019	https://voyant-tools.org/?corpus=931eb6e2e2b52d2c7ca4d2b808838b67&lang=en
2009-2019	https://voyant-tools.org/?corpus=d2e9c2adfd7cd4c6f038112ca32abdeb&lang=en

Year	Abstracts
1999	https://voyant-tools.org/?corpus=5d572d1b25974d94ba7cd3f0548214dc&lang=en
2000	https://voyant-tools.org/?corpus=e39e0fa31337267e121eebc2a0d9254f&lang=en
2001	https://voyant-tools.org/?corpus=bf5e602ddb8bc560391b674467a25dde&lang=en
2002	https://voyant-tools.org/?corpus=286280a8133eaa1a3ca6bdeb2eaea178&lang=en
2003	https://voyant-tools.org/?corpus=de714ed9caf7678f303237e343c78dbe&lang=en
2004	https://voyant-tools.org/?corpus=0b789e04bd2930e9dddadee13e029b55&lang=en
2005	https://voyant-tools.org/?corpus=3e0da4ed793dd720e6c3a4600c2793e3&lang=en
2006	https://voyant-tools.org/?corpus=b3baacdcae58e4554705eef3b3e26010&lang=en
2007	https://voyant-tools.org/?corpus=b37f4d60541dbe90ba771ebeb153fb27&lang=en
2008	https://voyant-tools.org/?corpus=8e9a266ddcb3b8c5c20a30399b4a8e4f&lang=en
2009	https://voyant-tools.org/?corpus=630d0691c0c569faeada6d0eb976877f&lang=en
2010	https://voyant-tools.org/?corpus=5d01f576e7bc3219aed0e7504fdde036&lang=en
2011	https://voyant-tools.org/?corpus=dd4d02553f7ff985e028b22790107da8&lang=en
2012	https://voyant-tools.org/?corpus=f949dd9bdc85ff1fe77a6e4d92ec7d91&lang=en
2013	https://voyant-tools.org/?corpus=834e1ccfafa1247bfce1e4b024cbdd10&lang=en
2014	https://voyant-tools.org/?corpus=c0b8bc83412125c84f3e087441a621b2&lang=en
2015	https://voyant-tools.org/?corpus=92cc0afb7420ef5173a673ea5413102f&lang=en
2016	https://voyant-tools.org/?corpus=3536962932bf17b66a0ca7b419b045f8&lang=en
2017	https://voyant-tools.org/?corpus=03538bc9efefa567630f1526b5aebf00&lang=en
2018	https://voyant-tools.org/?corpus=a5f080a1a83e832260b7fae894e9a738&lang=en
2019	https://voyant-tools.org/?corpus=847fa80afaace984be6224fb7a415065&lang=en
2009-2019	https://voyant-tools.org/?corpus=df301a90d6b9abd71674f256d12df318&lang=en

Regarding the year 1999, “electrical” and “bands” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. From this time, the major concern regarding polyaniline seemed to be how the electronic structure influences the electrical properties of the polymer. Several works dealt with this subject. Among them, one of the most relevant, cited 91 times, is the one from Professor Miroslava Trchová’s group (201). FTIR was used to study several polyanilines before and after protonation in the solid-state. The characteristic bands of the protonated or oxidized form were identified in the spectra of the materials. Analyses were made confirming the formation of quinoid rings during oxidation. Thus, the authors have made crystal the influence of the electronic structure and the oxidation state on the conductivity of the polymer.

In turn, from the year 2000, “nanocomposite” and “host” are the words from Titles and Abstracts, which present the highest correlations with the polyaniline term. This association can be understood as one of the first traces of the search for modification of the matrix and, consequently, of its properties via the inclusion of fillers, mainly nanostructured fillers, such as clay. A lot of scientific works dealt with these terms. Among them, one of the most relevant, cited 196 times, is the one from Professor Zongneng Qi’s group (202). The authors presented the synthesis and characterization of polyaniline/clay nanocomposites. This arrangement led to highly extended chains, through the insertion of PANi in the clay layers. The results allowed inferring that the majority of polyaniline chains were trapped between the clay layers. Besides, the extended chain shape was the result of the confined environment inside the nanometric galleries. This work has demonstrated the obtaining of highly conductive polyaniline via the physical arrangement of the polymer chains, being of unique importance.

Later, from the year 2001, “conductivity” and “enhanced” are the words from Titles and Abstracts, which present the highest correlations with the polyaniline term. A lot of scientific works dealt with these terms. Among them, one of the most relevant, cited 139 times, is the one from Professor Hyoungjin’s group (203). As the authors explained, polyaniline particles in their conductive form cannot be used directly in electro-rheological systems. Thus, seeking to enhance the rheological properties of the system under study, polyaniline was dedoped and then microencapsulated with melamine-formaldehyde resins. The authors proved that the flow stress of the fluid decreased with the increase in the amount of non-conductive resin used. Also, this effect was enhanced as the strength of the applied electric field increased, allowing the easy control the conductivity of the fluid without additional steps, which are very time-consuming. This work makes evident the concern with the processing of these conductive mixtures.

Regarding the year of 2002, “conductive” and “blends” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Polymer blending is a very efficient way to increase the maneuverability of polyaniline. Polyaniline blended with other polymers allows the construction of more elaborate artifacts, which are often essential components of several devices such as sensors and actuators. Lots of literature dealt with this subject. Among them, one of the most relevant, cited 152 times, is the one from Professor Masanobu Matsuguchi’s group (204). Here, the preparation of a gas ammonia sensor was the main objective. For this, the authors prepared blends of polyaniline and poly (methyl methacrylate). This blending increased the processability and physical properties of the conductive material. Preparation was made cheaper and more manageable compared to the electrochemical deposition technique. However, according to the authors, the results obtained have not yet been sufficient for the practical use of their sensing materials.

In turn, from the year 2003, “conducting” and “metal” are the words from Titles and Abstracts, which present the highest correlations with the polyaniline term. So, the retrieved data allow inferring that the major concern regarding polyaniline during this year was the search for materials that add the malleability of polymers to the conductivity of metals. The association of these properties allows imagining several applications, among them light coatings, which can act as Faraday cages. Among scientific works which dealt with these terms, one of the most relevant, cited 187 times, is the one from Professor Sundeep Dhawan’s group (205). Their article reports the preparation of polyaniline composites for shielding processes against electromagnetic interference. For this, the authors prepared blends of polyaniline, polystyrene, and polymethylmethacrylate. The prepared materials were effective in protecting from electromagnetic interference. Electromagnetic shielding applications are increasingly necessary in the modern world, where a myriad of frequencies is simultaneously used.

Later, from the year 2004, “based” and “acrylamide” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. As when higher values of electrical conductivity are pursued, the obtaining of water-soluble materials has encouraged the use of hydrophilic matrices for the preparation of materials useful in more sophisticated applications, as the active coating. Among the several works dealing with

this subject, one of the most relevant, cited 70 times, is the one from Professor Siddaramaiah Hatna's group (206). The authors presented an inverted emulsion process, used to the preparation of poly (aniline-co-acrylonitrile) conducting copolymers. The copolymers obtained are of high purity and have a crystalline nature. The solubility of the protonated form of poly (aniline-co-acrylonitrile) was confirmed. The improved solubility opens the door for a series of developments related to the field of paints and coatings. Among the possible hypotheses, the preparation of active surfaces, able to absorb radiation or even changing colors, becomes reachable.

Regarding the year of 2005, "doped" and "novel" are the words from Titles and Abstracts, which present the highest correlations with the polyaniline term. These keywords positively correlated with the term polyaniline serve as another indication of the growing search for new doped polymeric materials able to conducting electricity more efficiently. A lot of scientific works dealt with these terms. Among them, one of the most relevant, cited 91 times, is the one from Professor Tejjraj Aminabhavi's group (207). In their work, new polymeric membranes based on poly (vinyl alcohol) were filled with polyaniline nanoparticles. These membranes were used in the evaporative separation of water-isopropanol mixtures. The flow of the nanocomposite membranes was lower than that of the poly (vinyl alcohol) membrane. However, the selectivity of the nanocomposite membrane has increased considerably. Thus, the water-isopropanol mixture in the azeotropic composition was separated, which is impossible by simple distillation. Therefore, polyaniline can be useful in industrial processes for separating azeotropes.

In turn, from the year 2006, "dodecylhydrogensulfate" derivatives and "oxidation" were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Therefore, according to the retrieved data, one of the major concerning regarding polyaniline in this year was related to aniline polymerization in heterogeneous media. Again, lots of literature dealt with this subject. Among them, one of the most relevant, cited 103 times, is the one from Professor Dipak Khastgir's group (208). The authors prepared a stable aniline miniemulsion using sodium dodecyl sulfate as the surfactant. This type of heterogeneous system was, until then, very little studied. The use of stannous chloride produced a dramatic increase in the electrical conductivity of the system, mainly due to the extra formation of polarons. Besides, the heterogeneous system promoted an increase in the distance between polymer chains, which, consequently, reduced the crystallinity of the material. The more amorphous material presented an increased solubility, compared to conventional polyaniline. The contribution of this work is very relevant since the increase in the solubility of conducting polymers is one of the significant advances necessary for its wide diffusion in the most diverse semiconductor artifacts.

Later, from the year 2007, "hybrid" and "parameters" were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Therefore, according to the recovered data, the main concern on polyaniline was related to obtaining materials that more closely combined the individual properties of the starting constituents. Lots of literature dealt with this subject. Among them, one who represents this pursues, cited 10 times, and is the one from Professor Nicholas Pinto's group (209). In their relevant work, the authors studied the temperature dependence of a Schottky diode. This diode was manufactured from polyaniline nanofibers via electrospinning over an inorganic doped silicon substrate. This system, due to its elaborate architecture, allows the simultaneous existence of multiple charge transport mechanisms under normal operating conditions. This makes the system very interesting for electronic applications involving high-frequency circuits, which require a high working speed.

Regarding the year of 2008, "electrochemically" and "disordered" were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. The preparation of polyaniline via the electrochemical route produces material of higher purity, fewer defects, and more excellent conductivity. Even so, the insertion in these systems of disorderly agents, such as the randomly dispersed nanoparticles, can lead to new and improved physical and chemical properties. Among the literature dealing with this subject, one of the most relevant, cited 67 times, is from Professor Sundeep Dhawan's group (210). They reported, in a pioneering work, the synthesis of conducting and magnetic composites based on polyaniline. These composites were filled with maghemite nanoclusters. They were prepared via electrochemistry and chemistry. In both cases, the materials obtained produced very efficient electromagnetic shields. However, when the electrochemical polymerization of aniline occurred in the presence of nanoparticles, the shift of the electrochemical peak took place. This shift, associated with the increase in thermal stability of the materials obtained electrochemically, corroborates the hypothesis of the nanoparticles intimate incorporation in the polymer backbone. Despite being known at that time, Professor Dhawan's work shed new light

on the magnetic properties of the polyaniline systems. One of the possible consequences of this magnetic properties improvement lies in the construction of new devices capable of storing data more efficiently.

In turn, from the year 2009, “nanofibers” and “phosphate” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. The increasingly abundant supply of nanofibers, including carbon ones, as well as the improvement of polymerization in the presence of ionic liquids, allowed the preparation of new materials with unique adhesive properties. As in the previous cases, lots of literature dealt with this subject. Among them, one of the most relevant, cited 87 times, is the one from Professor Huangxian Ju’s group (211). The authors, in a breakthrough work, prepared nano fibril composites based on polyaniline and carbon nanotubes. These materials were prepared in the presence of ionic liquid. They were used in the construction of a phenol sensor. The development of the sensor was done via the immobilization of tyrosinase on the material surface. Surprisingly, the carbon nanofiber acted as a molecular model, guiding the growth of polyaniline on its surface. This growth mechanism resulted in extreme adhesion between the phases. The prepared sensor showed excellent amperometric performance in the detection of phenol compounds. Also, according to the authors, the described experimental approach has great potential for multiple applications in electrically active devices.

Later, from the year 2010, “development” and “NaCl” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Sodium chloride is beneficial in the synthesis of polyaniline, where it works by increasing the density and conductivity of the continuous phase. In typical applications, NaCl is handy as a corrosive agent in anti-corrosion tests. Several works dealt with this subject and, one of the most relevant, cited 57 times, is the one from Professor Xavier Perrin’s group (212). In their relevant work, the authors tested the anti-corrosive performance of mild steel sheets. Therefore, these plates were coated as a blend of plasticized chlorinated rubber and polyaniline. The materials were tested using salt spray and immersion in NaCl solution. Regarding protection against corrosion, the results obtained proved the superiority of the polyaniline-based coating compared to traditional zinc phosphate-based coatings. The authors stated that the protection mechanism of polyaniline is complex. Despite this, they proposed that the high electroactivity of polyaniline in the form of emeraldine salt is responsible for the observed anodic protection. The results presented are promising and superior to conventional treatments, indicating that this type of new polymeric material can be an economically viable alternative to improve anti-corrosion processes.

Regarding the year of 2011, “hydrogen” and “carried” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Hydrogen peroxide works as a low-efficiency oxidizing initiator for the chemical synthesis of polyaniline (213). In turn, depending on the form of preparation, polyaniline can function as a carrying system capable of detecting hydrogen peroxide. The quantification of hydrogen peroxide is of great importance for the food industry, where this chemical specie is used as an antibacterial agent for the preservation of milk (214). Several works dealt with this subject and, one of the most relevant, cited 95 times, is the one from Professor Jianbin Zheng’s group (215). Here, the authors presented a novel sensor for the detection of hydrogen peroxide. This device was based on the deposition of polyaniline, induced by horseradish peroxidase, on graphene nanoparticles/carbon nanotube/gold-platinum alloy. The measurements of square wave voltammetry allowed inferring a detection limit of the order of 10^{-7} M. According to the authors, when the prepared sensor is compared to other sensors, the detection response is faster, of higher sensitivity, besides presenting a lower detection limit. These results are promising, and the development of highly selective electrochemical biosensors may be the basis.

In turn, from the year 2012, “graphite” and “deposited” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Graphite, carbon black, and, more recently, graphene are widely studied structures in association with polyaniline. Each of them has the potential to dramatically modify the properties of the material, improving its mechanical and electrical performance. Among the literature dealing with this subject, one of the most relevant, cited 131 times, is the one from Professor Guangshi Tang’s group (216). In their work, exfoliated graphene oxide (GO) and polyaniline composites were prepared via *in situ* polymerization. The results demonstrate the existence of strong interactions between graphene oxide and polyaniline, including electrostatic forces, hydrogen bonding, and π - π stacking. The improved thermoelectric properties of the resulting material provided increased mobility for charge carriers. In this context, the material presented is a promising candidate for thermoelectric applications. In this case, the generation of electric energy through the capture of heat continues as

one of the most significant challenges that modern science faces to increase the quality of life of our growing world population.

Later, from the year 2013, “nanostructured” and “exfoliation” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. These themes are connected and complement each other, mainly in the field of energy storage. Capacitive energy storage has received much attention since it has the potential to replace conventional devices very efficiently with lower environmental impact. A lot of literature dealt with this subject and, among them, one of the most relevant, cited 150 times, is the one from Professor Wei Feng’s group (217). In this work, the authors synthesized exfoliated graphene oxide/polyaniline composites via electrodeposition. The capacitance of the exfoliated nanocomposite was about 120% higher than that of polyaniline. According to the authors, the insertion of graphene oxide in the polymeric matrix produced three-dimensional nanostructures. These structures allow easy access for charge transfer and ion transport throughout the electrode. The results suggest that these nanocomposite materials are up-and-coming for high-performance supercapacitors.

Regarding the year of 2014, “electrode” and “exposed” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. The concern with electrodes and the exposure of these materials and constituents was a trend this year. Among the works dealing with this subject, one of the most relevant, cited 260 times, is the one from Professor Vincent Gomes’s group (218). The subject involving supercapacitors arose again. In this work, the authors produced composite films based on nanostructured graphene oxide and polyaniline. The flexible film produced was tested and showed results statistically superior to those presented by polyaniline. The significant contribution of the authors in this work was the presentation of a scalable synthesis route, which is suitable for the industrial production of nanostructured electrodes, allowing the diffusion of the material for several potential applications in this very relevant field.

In turn, from the year 2015, “characterization” and “monomer” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Thus, according to the retrieved data, the concern about fundamental aspects in the field of polyaniline has returned. More than that, the search for new ways of using aniline to facilitate its integration in more complex structures seems to have dominated the scene this year. Several works dealt with this subject. Among them, one of the most relevant, cited 20 times, is the one from Professor Ahmed Youssef’s group (219). The authors have prepared nanocomposites based on polyaniline, filled with montmorillonite clay via *in situ* polymerization. They used a heterogeneous medium. The authors very intelligently reacted aniline with hydrochloric acid. The aniline hydrochloride was used as a modified monomer. This monomer allowed the cation exchange with the sodium ion of the basal spaces of the clay. In comparison with the analog prepared with aniline, the results showed an increase in the conductivity when the nanocomposite was developed using the modified monomer. From our humble point of view, the most significant contribution of the work resides in the demonstration that small modifications in the monomers can result in nanosystems with better properties. In other words, the return to the base chemistry allows exploiting changes that can promote the increase of features of interest with relatively fewer efforts.

Later, from the year 2016, “acids” and “chloroform” are the words from Titles and Abstracts, which present the highest correlations with the polyaniline term. Again, the search for studies that improve the base understanding of conducting systems and how they can be improved lead the research in this year. A lot of scientific works dealt with these terms and, among them, one of the most relevant, cited 16 times, is the one from Professor Anwar ul Haq Ali Shah’s group (220). The authors studied changes in the synthesis of polyaniline in the presence of polyvinyl alcohol. The authors worked with a heterogeneous polymerization system in a reverse emulsion. The results showed that, in addition to the excellent electrical conductivity, the materials obtained were soluble in common organic solvents, including chloroform. They also reported that the morphology of the blends had pores of irregular and unequal sizes, being an electroactive material, based on electrochemical measurements. Results have shown that, in a certain way, the scientific community decided or sought to mature and reinforce the fundamental knowledge about this material. Contrary to being a setback, this type of return to the roots of the theme shows that the construction of base knowledge is a fundamental step for more in-depth advances in the field in question.

Regarding the year of 2017, “anti-corrosion” and “performed” were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Once again, the anti-corrosion properties and performance of polyaniline and its derivatives gained prominence, allowing us to perceive that the focus of the works returned to the field of applications. Among the works dealing with this subject, one of the most relevant, cited 11

times, is the one from Professor Zhiming Zhang's group (221). The authors focused on the preparation of anti-corrosive coatings. These coatings were based on a hydrophobic double-layer material, which was composed of polystyrene under a blend of polyaniline and polymethylmethacrylate. Carbon steel was covered with the protective layer and was then immersed in a NaCl solution. The results showed that the coating system prepared by the spray method produced the best anti-permeability associated with excellent protection against corrosion. This excellent protective performance was due to the anodic protection of the primer composed of polyaniline and polymethylmethacrylate. The specificity of the theme addressed by the authors demonstrates the return to more practical questions that involve markets of gigantic size, where new materials can displace old products, creating excellent opportunities for further profitable businesses.

In turn, from the year 2018, "oxidation" and "interaction" were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Thus, according to the retrieved data, the correlation analysis showed that the theme that marked the year 2017 remained highlighted in 2018. Several works dealt with this subject and, one of the most relevant, cited 28 times, is the one from Professor Bahram Ramezanzadeh's group (222). The authors have modified nanoparticles of graphene oxide using polyaniline nanofibers and zinc cations by a layer-by-layer assembly method. In addition to various physical measurements, according to the authors, the theoretical results derived from quantum mechanics calculations revealed that inorganic zinc cations underwent electrostatic and β -cation interactions with polyaniline, implementing and strengthening the bond between zinc and polyaniline. Thus, in addition to the results of electrochemical impedance that demonstrated the efficiency of the new material produced, the authors offered a solution for the experimental observations, based on quantum mechanics. So, we can believe that the advances in the manufacture of increasingly powerful microcomputers will make this type of association more frequent and, finally, essential for future scientific work involving complex systems based on polyaniline.

Finally, from the year 2019, "nanocomposites" and "PD (power density)" were the words from Titles and Abstracts, which presented the highest correlations with the polyaniline term. Here, the themes related to very particular subjects returned to the scene. In particular, the demand for nanocomposites associated with an increase in the power density of the energy storage devices. Lots of literature dealt with this subject. Among them, one of the most relevant, cited 4 times, is the one from Professor Syed Shahabuddin's group (223). Here, the authors reported, in their own words, a simple way for the production of polyaniline flakes embedded in SrTiO₃ nanocubes. They prepared this nanocomposite by *in situ* oxidative polymerization. The composite system obtained has an energy storage capability higher than that observed for each of the constituent materials individually. Besides, the authors produced a supercapattery (a word meaning super-capacitor + battery). This supercapattery was based on the presented nanocomposite associated with activated carbon. The performance of the device was excellent due to the combined effect of the nanocomposite with activated carbon. Also, the cyclic analysis of the manufactured supercapattery revealed the improved and durable stability of the device even after thousands of charge and discharge cycles. Once more, the search for innovative, more efficient, safe, cheap, and long-lived ways to store energy is a sincere concern. We do believe that this subject should guide many studies in the coming decade.

Finally, the data contained in the titles and abstracts were combined year by year and submitted for analysis by Voyant Tools. The most common and relevant terms were selected for the preparation of the respective trend curves, which were gathered in Figure 3. The terms selected were generalized using the Voyant Tools' asterisk (*) function. This procedure allowed us to investigate the variations in each term. So, for instance, the term "model *" includes model, models, modeling, etc.

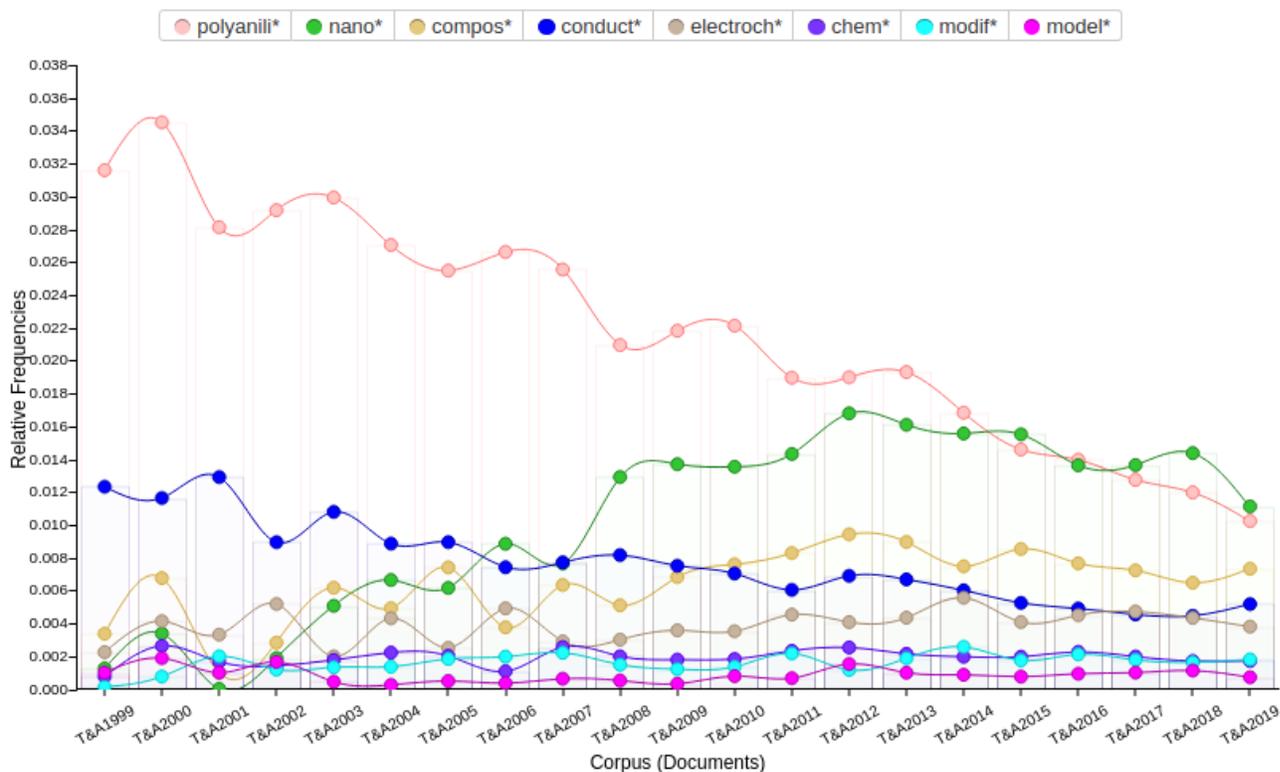


Figure 3 – Trends of the main terms from combined titles and abstracts between 1999 and 2019, available at <https://voyant-tools.org/?corpus=a48f340669dff51600aa5742628b5d4b>

The abscissa of Figure 3 shows the corpus of the collected documents. The ordinate, in turn, shows the relative frequencies. These trends are all computed and stored on the Voyant Tools website. As expected, the term “polyanili*” is the one with the highest relative frequencies over most of the analysis time. The relative frequency of the term polyaniline declines over time. This drop is probably the result of more and more specific and frequent applications of this polymer material. Thus, the term “polyanili*” is gradually being complemented by other terms that add relevance and value to it.

An example of this complementation is the term “nano*”. As shown in Figure 3, this term has gained relevance over the years. Besides, its relevance in 2016 was practically equal to the one of the term “polyanili*”, surpassing it in the years 2018 and 2019. This rise is undoubtedly the result of the increasing understanding of the ability to modify the properties of host materials imparted by properly engineered nanoparticles.

Another relevant term that has gained importance over the years is the term composite (“composi*”). The term electrochemistry (“electroch*”) also shows an upward trend. In turn, the term conductivity (“conduct*”) shows a downward trend, probably due to the many new applications of this conductive polymer. The other relevant terms are chemistry (“chem*”) and modification (“modif*”). These terms have maintained their relative frequencies over the years, indicating their importance and relevance. Although with lower relative frequencies than the other terms, the term modeling (“model *”) shows an upward trend over the past few years. This increase in relevance is expected to be increasingly prominent in the coming years, especially when we consider the cheapness and increased processing capability of modern computers.

4. Conclusions and perspectives

The data collected here through Text Mining tools leads us to the conclusion that the study of the polyaniline theme is far from reaching its term. More than that, the correlations showed throughout this research indicate an evolution of studied systems, both in quality and sophistication. These systems are a clear result of studies and understanding of these materials on the nanoscale, which has opened up new perspectives for previously unsolved problems. Among these problems, issues related to corrosion protection and energy storage are worth mentioning.

To our minds, these themes will be drivers for research in the coming decades and that they will be significantly expanded with the advances that will come from Nanotechnology and Molecular Modeling. As a final challenge, we must not forget that Picotechnology (art that involves the manipulation of species on the scale of 10^{-12} m), is fundamental for the advancement of studies related to the field of polyaniline, via modification and improvement of specific chemical properties, which can be done, among other ways, by conjugating polyaniline with several other compounds existing in nature. This dive in Picotechnology, Nanotechnology, and Molecular Modeling is the catalyst for accelerating the arrival of the Fifth Industrial Revolution, where machines, systems, and people will work together, making results more efficient and processes, increasingly strategic. As an extra benefit, this new revolution will drive away the fear arising from the Fourth Industrial Revolution, according to which technology would take millions of jobs. To our minds, realizing that polyaniline, pioneering reported by Letheby in 1862, has all the potential to be a crucial part of this thrilling future history. As a final call, we hope you enjoy and take part of this future!

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Credit author statement

Fernando G. de Souza Junior: Conceptualization, Methodology, Data analysis, Writing-Original draft preparation, Conceptualization, Supervision, Reviewing and Editing

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