

# Bibliometric survey of the PVC production – Part I: the continuous polymerization challenge

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## Abstract

Poly(vinyl chloride) (PVC) resins constitute the third most important plastic materials available commercially, in terms of worldwide volume production, and can be manufactured through several polymerization mechanisms, including free radical, ionic and redox polymerization processes. Approximately 80% of the worldwide commercial PVC production is performed through suspension polymerization processes in batch mode, due to intrinsic problems of continuous suspension polymerization processes, such as polymer incrustation in reaction vessels, transport equipment and pipes. For this reason, the present review provides an extensive bibliometric survey, including papers and patents, on attempts to develop continuous polymerization process technologies for PVC manufacture. Particularly, the present survey characterizes the degree of maturity and the main bottlenecks of continuous PVC processes that have been frequently overlooked in the technical literature.

**Keywords:** PVC, continuous polymerization, suspension polymerization, bibliometry.

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## 1. Introduction

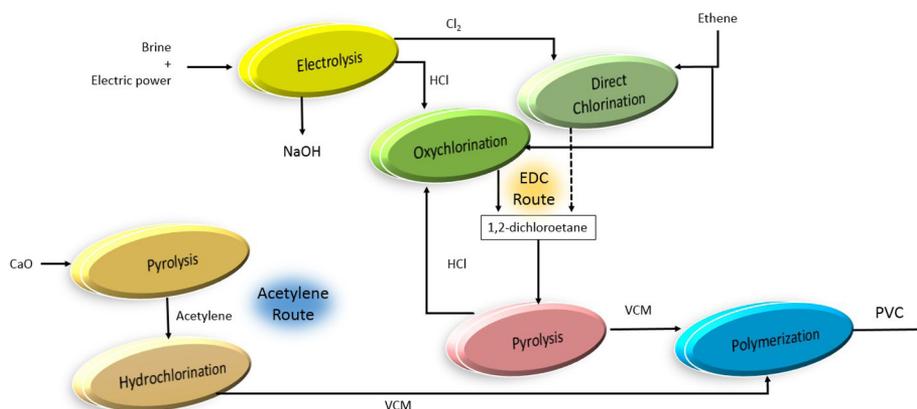
Poly(vinyl chloride) (PVC) belongs to the group of the most important commercial plastic materials, being surpassed only by polyethylene (PE) and polypropylene (PP) in terms of worldwide volume production<sup>[1]</sup>. For example, in 2016 the global PVC production capacity reached 61 million metric tons<sup>[2]</sup>. Besides, the global PVC market was expected to grow from 24.39 billion dollars in 2020 to 29.56 billion dollars in 2021, representing an annual growth rate (CAGR) of 21.2%<sup>[2]</sup>. As a matter of fact, PVC has been widely used in many distinct areas, including building<sup>[3]</sup>, construction<sup>[4]</sup>, transportation<sup>[5]</sup>, packaging<sup>[6]</sup>, electrical<sup>[7]</sup>, and healthcare applications<sup>[8]</sup>, although commercialized with different commercial names, such as rigid PVC, flexible PVC and PVC film. In the construction industry, PVC is regarded as one of the most significant materials, consuming almost 50% of the commercially available PVC resins<sup>[9]</sup>. For instance, one can find PVC pipes and tubing in several civil engineering applications that include water supply, drainage, and electrical conduits.

PVC is manufactured through polymerization of vinyl chloride monomer (VCM) and Figure 1 schematically represents the usual PVC production chain from raw materials.

The purification steps were omitted from Figure 1 for the sake of conciseness. Based on the proposed scheme, one can observe that the PVC business depends on the petrochemical industry for the supply of ethylene, but also on the chlor-alkali industry for supply of chlorine (from brine), another primary feedstock for the PVC production process.

PVC was originally discovered, accidentally, by the chemist and physicist H.V. Regnault, in 1838, who was also responsible for the first synthesis of vinyl chloride in collaboration with von Liebig, in 1835. Then, chemist E. Baumann also synthesized PVC years later in 1872, explaining why both investigators are normally considered responsible for the discovery of PVC<sup>[10]</sup>.

The commercial production of PVC started in Germany in the 1930's and the onset of the war (1939-1945) fueled its demand<sup>[11]</sup>. Nowadays, it is well-known that PVC can be synthesized through several polymerization mechanisms, including free-radical (most common commercially)<sup>[12]</sup>, anionic<sup>[13]</sup>, cationic<sup>[14]</sup> and redox polymerization mechanisms<sup>[15]</sup>. For example, Table 1 illustrates the main mechanistic steps when the free-radical technique is used for manufacture of PVC.



**Figure 1.** Schematic representation of the PVC production chain.

**Table 1.** Typical free-radical vinyl chloride polymerization mechanism.

Mechanism Step	Reaction
Initiation	$I \xrightarrow{k_d} 2I^* \quad I^* + M \xrightarrow{k_i} R_1$
Propagation	$R_n + M \xrightarrow{k_p} R_{n+1}$
Transfer to monomer	$R_n + M \xrightarrow{k_{tm}} P_n + R_1$
Transfer to polymer	$R_n + P_m \xrightarrow{k_{tp}} P_n + R_m$
Termination by combination	$R_n + R_m \xrightarrow{k_{tc}} P_{n+m}$
Termination by disproportionation	$R_n + R_m \xrightarrow{k_{td}} P_n + P_m$

$I$ : initiator;  $I^*$ : initiator fragment;  $M$ : monomer;  $R_i$ : free-radical growing chain of size  $i$ ;  $P_i$ : dead polymer chain of size  $i$ ;  $k_d, k_p, k_{tm}, k_{tp}, k_{tc}, k_{td}$ : kinetic rate constants.

Regarding the production processes, PVC can be produced through mass or bulk, suspension, emulsion and solution polymerizations, mostly in batch or semi-batch modes. However, almost 81% of the PVC produced commercially worldwide are based on suspension polymerization processes<sup>[16]</sup>. Nevertheless, to this date, no feasible commercial suspension processes can be operated in continuous mode, mainly due to intrinsic problems of the suspension polymerization process, such as polymer incrustation (fouling) in transport equipment and pipes.

Based on the previous paragraphs, the main objective of the present work is to present an extensive bibliometric survey, including papers and patents, on PVC process technology. Particularly, it is intended to report the maturity and the main bottlenecks of continuous suspension PVC polymerization processes that have been frequently overlooked in the technical literature. Before diving into the bibliometric survey, a brief description of reaction mechanisms and processes are provided.

## 2. PVC Polymerization

### 2.1 Free-radical mechanism

At the industrial level, PVC is produced mostly through free-radical polymerizations (FRP)<sup>[17]</sup>. A typical FRP mechanism includes many fundamental reaction steps, as shown in Table 1. As a matter of fact, several investigators studied the kinetic aspects of vinyl chloride polymerization and proposed detailed mechanisms that consider many other additional fundamental steps, needed to describe the final properties of the PVC resin<sup>[18-20]</sup>. Particularly, among the many monomers that can polymerize through FRP, vinyl chloride stands out for showing characteristically high kinetic rate constants for transfer to monomer<sup>[21]</sup>. In fact, this characteristic explains why the average chain length of the polymer material (the number-average molar mass of commercial PVC grades usually ranges from 50 kDa to 100 kDa) is controlled by the reaction temperature. Moreover, the termination reactions occur mostly by disproportionation<sup>[22]</sup>.

### 2.2 Bulk process

The bulk or mass polymerization process can be regarded as the most elementary polymerization technique, as the pure monomer (or mixture of comonomers) and one or more suitable initiators are mixed and used as reactants, leading to a final product that contains a mixture of residual unreacted monomer and the produced polymer<sup>[21]</sup>. As a matter of fact, the necessity of fewer purification steps constitutes one of the greatest advantages of the bulk process<sup>[23]</sup>.

Two industrial processes have been commonly used to perform the bulk polymerization of vinyl chloride: the single-stage and the two-stage polymerization processes<sup>[11]</sup>. In both cases, a mixture of VCM and initiator is fed into the reaction vessel and heated to the desired reaction temperature in order for the polymerization reaction to take place. However, in the two-stage process the reactor content is transferred to a second vessel when conversion reaches approximately 10%, leading to conversions around 85-90% in the second vessel<sup>[23]</sup>. As PVC is not soluble in its monomer, a third phase (besides the liquid and gas phases) appears after about 2% of conversion<sup>[20,24]</sup>. Therefore, in the two-stage process the first reactor is used to produce

the PVC polymer seeds for better control of the particle morphology. An important aspect of the bulk polymerization technology is related to the removal of the heat released by reaction. Inefficient mixing combined with poor heat removal can lead to development of hot spots, posing important control and safety issues to the operation<sup>[21]</sup>. At the end of the reaction, the PVC resin is obtained in the form of spherical polymer particles with diameters ranging from 50 to 150  $\mu\text{m}$  and with high porosity<sup>[23]</sup>. The difficulty to manipulate the morphological features of the final polymer powder constitutes a major drawback of this process and can explain why the suspension polymerization process became so popular in the industrial field.

### 2.3 Solution process

The solution polymerization of VCM is not employed industrially very frequently<sup>[25]</sup>, as an organic solvent must be removed to recover the PVC resin. As a matter of fact, the use of solvent imposes the implementation of multiple purification steps, to recover the resin and the residual monomer and to recycle the solvent, leading to additional equipment and operational costs<sup>[23,26]</sup>. Despite that, the solution process can present some competitive advantages when compared to the bulk process. Firstly, the solvent can make the removal of heat easier; secondly, the solution (or dispersion, if the polymer is not fully soluble in the solvent) viscosity can be lower during the reaction, demanding less energy for mixing<sup>[21]</sup>. From the chemical standpoint, chain transfer to solvent may also take place, reducing even further the average molar mass of the polymer product<sup>[27]</sup>. Finally, the PVC particles are obtained in the form of spherical polymer particles with diameters ranging from 50 to 150  $\mu\text{m}$  and with high porosity<sup>[23]</sup>, although the morphological features of the product are difficult to manipulate, reinforcing the competitive advantages of the suspension polymerization processes.

### 2.4 Emulsion process

Emulsion and suspension VCM polymerizations share some subtle similarities, in the sense that both are performed in the presence of a dispersed monomer phase. However, as thoroughly discussed in the literature, there are some important differences related to the particle size, type of initiator, particle nucleation mechanism and dependence of reaction rates on reaction parameters<sup>[21]</sup>. First, polymer particles obtained through emulsion polymerizations are much smaller, with typical sizes lying on the nanometric scale (typically 100 to 500 nm) and forming a stable latex. Polymer particles are formed after nucleation of monomer swollen surfactant micelles by free radical fragments produced by aqueous soluble initiators, such as potassium persulfate, and under continuous strong agitation<sup>[23]</sup>. The monomer feed usually lies in the range 30–46 wt%, so that the presence of water makes thermal and viscous effects much less relevant than in the bulk process, which also makes the process control easier<sup>[21]</sup>. However, the energy demanded to separate the very fine PVC particles can be extremely high, justifying the commercialization of the latex as the final polymer product<sup>[11]</sup>. Indeed, PVC latexes have been widely used for manufacture of films, adhesives and covering of hard and soft surfaces, representing 15% of the PVC commercial market.

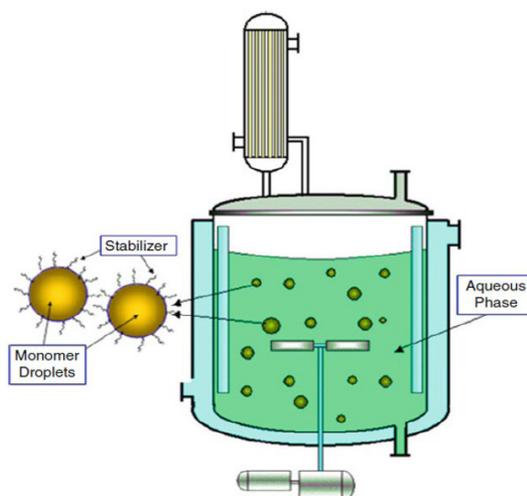
### 2.5 Suspension process

It is estimated that 80% of the PVC produced worldwide is obtained through batch suspension polymerizations, making this the most important PVC polymerization process<sup>[16]</sup>. Figure 2 shows a general schematic representation of a typical suspension polymerization process, which makes use of large batch stirred tank reactors, so that the heat removal capacity is of paramount importance to guarantee the safety of the industrial plant operation<sup>[28]</sup>.

In standard suspension polymerizations, the initial reacting mixture (a mixture of monomer and oil soluble initiators) is suspended in water (through suitable combination of agitation speed and addition of suspending agents) and heated until the desired reaction temperature, where the polymerization reaction occurs. Contrary to the emulsion process, the polymer chains are then formed inside the previously dispersed monomer droplets. From a microscopic point of view, one can assume that each dispersed monomer droplet acts as a small bulk reactor. For this reason, the bulk and suspension processes present very similar kinetic features<sup>[27,29]</sup>.

Particularly, the presence of the suspending aqueous phase improves the heat removal from the reacting mixture and reduces the effective viscosity of the dispersion<sup>[30]</sup>, also allowing production of spherical polymer particles with characteristic diameters ranging from 10 to 500  $\mu\text{m}$ <sup>[29]</sup>. It is important to notice that manipulation of both agitation and surfactants (type and amounts) can allow the control of the particle morphology, which is very important for commercial purposes and partially explains the success of this technology. Indeed, the particle porosity plays an important role in the final application of the resin, since it controls the rates of plasticizer adsorption and the interaction of the resin with the plasticizers, affecting the performances of processing stages and the final properties of PVC pieces<sup>[31]</sup>.

For the previously discussed reasons, many efforts have been made to develop commercially feasible continuous PVC suspension polymerization processes, although inherent process characteristics have prevented the successful



**Figure 2.** General schematic representation of a suspension polymerization reactor.

industrial operation of continuous processes so far. In this context, technological attempts, existing bottlenecks, and some future perspectives for development of continuous PVC suspension polymerization processes are discussed in the following sections.

### 3. Data Source and Methodology

#### 3.1 Initial searches

Initially, a top-down searching approach was employed, where the initial searches were used to provide general overviews of the investigated technologies and the subsequent searches were performed to narrow down the scopes of the analyzed fields. The performed surveys were focused mainly on the continuous production of PVC, on continuous suspension polymerization processes and on the main commercial processes used worldwide by the PVC industry. The investigations were performed with the help of electronic search tools including *Web of Science* (for papers) and *EspaceNet* (for patents). The following keywords were used to perform the initial searches:

- Search 1 – “*suspension AND polymeri?ation AND (PVC OR polyvinyl chloride OR poly(vinyl chloride) OR poly vinyl chloride)*”;
- Search 2 – “*continuous AND suspension AND polymeri?ation*”;
- Search 3 – “*continuous polymeri?ation AND (PVC OR polyvinyl chloride OR poly(vinyl chloride) OR poly vinyl chloride)*”.

For patents, a filter was used for the Cooperative Patent Classification (CPC) and the International Patent Classification (IPC) fields (C08) in order to refer to “*organic macromolecular compounds, its preparation or chemical processing and compositions based on them*”. Additionally, the search filter for keywords in the title or in the summary of documents was used. Considering the search of papers, the query was applied to the topic filter, which is a special filter from *Web of Science* that can be applied to title, abstract, author keywords, and Keyword Plus®. The data analysis of papers for clustering visualization was made using the software VOSViewer (version 1.6.18).

Thus, the main objective of the proposed procedure was to prioritize works that, in fact, were related to the production methods and respective processes, discarding research on either product processing or new applications. More specifically, Search 1 aimed to identify technical innovations related to the PVC suspension production process. In addition, Search 2 was conducted to investigate innovations related to the continuous suspension polymerization process, regardless the produced polymer. Search 2 assumed that methodologies used successfully to produce other polymers through suspension polymerizations might be eventually extended for PVC, after necessary improvements/adaptations. Finally, Search 3 intended to characterize innovative activities related to the continuous suspension polymerizations of VCM. The obtained results are reported in the following sections, including the general statistical analyses of the obtained data.

#### 3.2 Types of processes (bulk, solution, emulsion, suspension)

For better assessment of the current technological status of PVC manufacture, searches were targeted at the different types of industrial PVC production processes. This subdivision can be justified by the fact that different processes demand the use of different technologies due to the intrinsic features of each process. Additionally, clustering the data in accordance with the production processes favors the interpretation and analysis of available data. For this reason, after finishing the initial searches, additional filters were applied to group the obtained references in the form: (i) bulk – “*bulk polymeriz\* OR bulk polymeris\* OR mass polymeriz\* OR mass polymeris\**”; (ii) solution – “*solution polymeriz\* OR solution polymeris\**”; (iii) emulsion – “*emulsion polymeriz\* OR emulsion polymeris\**”; and (iv) suspension – “*suspension polymeriz\* OR suspension polymeris\**”.

### 4. Results and Discussion

#### 4.1 Initial search from patents

After Search 1, 365 documents were found. Figure 3 depicts the distribution of patents from 1932 to 2021. Between the 1960s and 1980s there was significant increase of patent application activity in the field, most likely due to the development of PVC stabilization technologies and the growing PVC use in civil construction applications<sup>[32]</sup>. From the 1980s, it is possible to observe a clear trend to reduce the number of documents published per year, a fact that can be explained by the technological maturity of the PVC production technologies and publication of studies that indicated the VCM toxicity to human health<sup>[32]</sup>. These studies reported that VCM might be associated with angiosarcoma (a type of cancer in the liver) and that PVC dust inhalations might cause cancer of the lung and other organs<sup>[33]</sup>. However, the number of patents has substantially increased again since 2015, due to the fast development of PVC plasticizer technology and increasing demand for PVC in China (51 Chinese patents out of 59 deposited documents in the period). This Chinese interest in PVC has been strongly correlated with the growing internal demand associated with the construction activity in China<sup>[34]</sup>.

Figure 4 reports the number of patents filed in each priority country. A concentration of documents can be perceived in China, United States, Germany, and Japan,

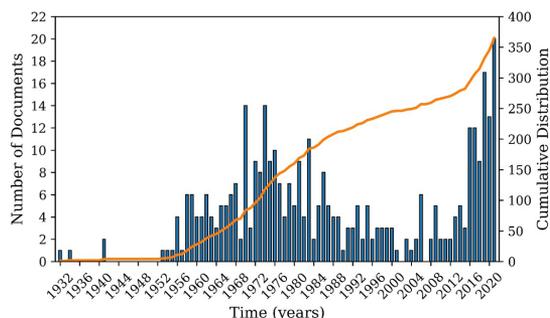


Figure 3. Annual production of patents as found in Search 1.

which are the countries of origin of the main market players and where the PVC production volumes are the largest in the world. Figure 5 reports depositors identified in the first search. Only companies that deposited 8 or more patents are described for the sake of conciseness. It can be observed that Solvay (Belgium) stands out with 35 deposited patents, many of them coming from companies acquired by Solvay, such as Satuffer Chemicals (USA) and Rhone Poulenc (France). Evonik Industries AG (Germany) also acquired some important companies, including Werke Hüls (Germany) and Degussa (Germany), being the second largest depositor. Shin-Etsu (Japan) and LG Corporation (South Korea) are also important Asian players, a region that has shown considerable growth since the 1990s. Particularly, LG deposited its first document in 2003, being the largest depositor in recent years.

In Search 2, 225 documents were found. Figure 6 reports the number of patents deposited between 1946 and 2021 about the development of continuous suspension polymerization processes. It can be observed that the interest in the analyzed subject has remained practically constant over the years and that the patents were filed mostly in the United States, Germany, Japan, and the United Kingdom, as shown in Figure 7. It must be observed that the patent leaders listed in Figures 4 and 7 are essentially the same, which suggest a close relationship between the two analyzed subjects:

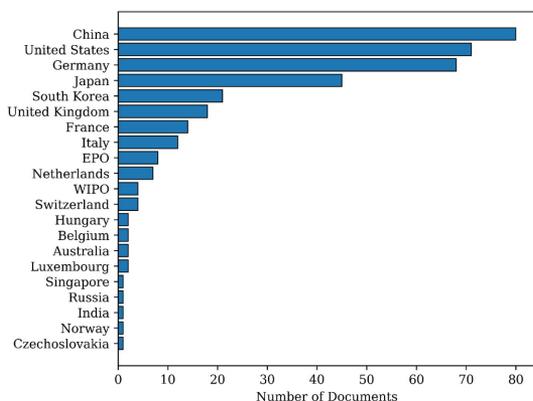


Figure 4. Distribution of patent documents per country as found in Search 1.

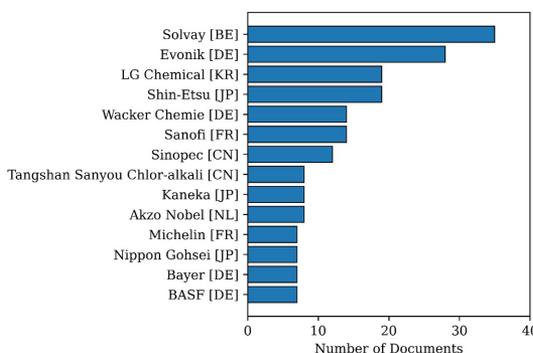


Figure 5. Distribution of patents in the most productive institutions as found in Search 1.

interest in developing PVC technologies and continuous suspension polymerization processes.

Figure 8 reports the most active depositor companies in the field of continuous suspension polymerizations. It can be observed that the scenarios presented in Figures 5 and 8 are quite different, clearly indicating that innovative activity in the field of continuous suspension polymerizations is not driven by the PVC market, as suggested in the previous paragraph. It is also interesting to observe that traditional

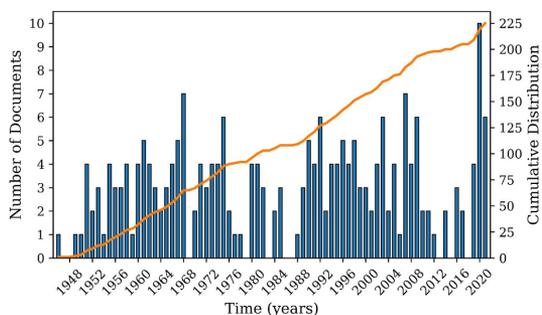


Figure 6. Annual production of patents as found in Search 2.

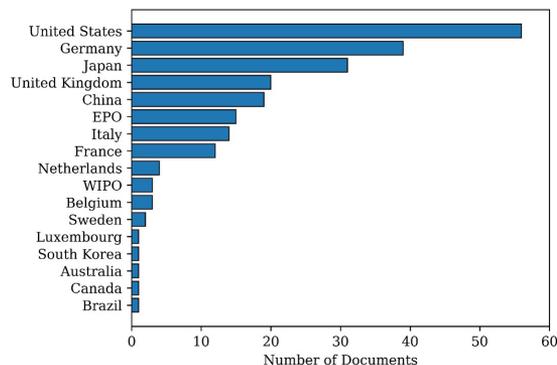


Figure 7. Distribution of patent documents per country as found in Search 2.

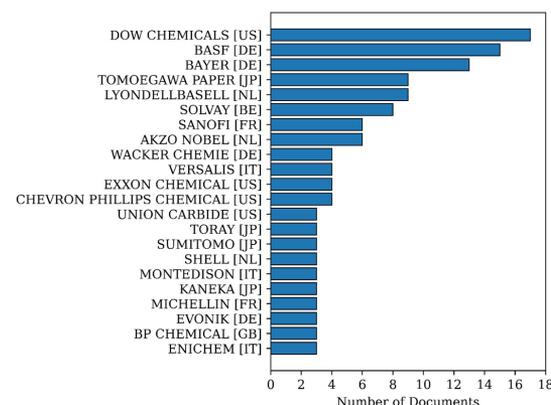


Figure 8. Distribution of patents in the most productive institutions as found in Search 2.

chemical companies, such as Dow Chemical Co. (USA), Bayer (Germany) and LyondellBasell (Netherlands), have developed many technologies for production of suspension polymer powders that are not related to PVC.

In Search 3, 15 documents were found. However, after analyzing the patents, it was found that only five of them were related in fact to developments of continuous PVC suspension polymerization processes. Bubsy<sup>[35]</sup> (patent by Imperial Chemical Industries, GB, now Akzo Nobel, NL) developed a process for producing porous PVC particles in continuous, batch or semi-batch systems. According to the author, when the process is operated continuously, it is preferred to feed VCM to the reactor in gaseous form to avoid polymer accumulation on the reactor walls. The author also reports that the obtained particles may present a wide size distribution with many fine particles. The most important claim of the patent was the design of the reaction vessel, which comprised two concentric chambers separated by a solid wall, so that the organic dispersion was forced to flow through two effective reactors connected in series, to narrow the residence time distribution and, consequently, also the particle size distribution. Following a similar line of thought, Dirix et al.<sup>[36]</sup> (patent from Akzo Nobel, NL) claimed a VCM suspension polymerization or copolymerization process that can be conducted continuously in a series of continuous stirred tank reactors (CSTRs). The authors reported that 2 to 5 CSTRs should be used in the series, although the last reactor of the series should be operated in batch mode to complete the reaction.

Kircher Jr. et al.<sup>[37]</sup> (patent from Detrex, US) developed a continuous VCM suspension polymerization process based on two jacketed CSTRs connected in series, characterized using a mixing device to prepare the suspension that was fed into the first vessel of the series and by the partial recirculation of the organic dispersion produced in the vessels. The authors reported that such proposed reaction scheme allowed the enhanced control of the particle size distributions and reduction of polymer fouling on the reactor walls and accessories. Klippert et al.<sup>[38]</sup> (patent from Hoechst, DE) also proposed the use of a set of multiple reactors in series (in this case, 3 tubular reactors) to perform the continuous polymerization of VCM. The authors claimed that the proposed design of the internal walls and accessories and a particular positioning and geometrical features of the reaction vessels allowed the narrowing of the particle size distributions and reduction of polymer fouling.

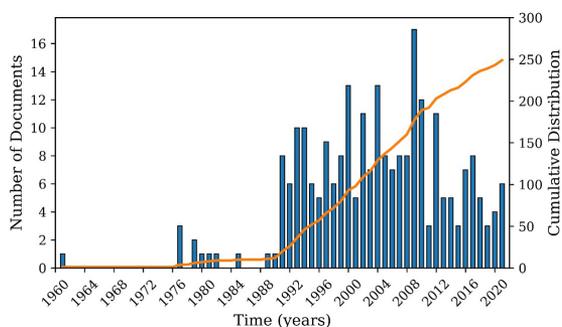
Weibin et al.<sup>[39]</sup> (patent from Huayang New Material Tech Group Co., CN) proposed a scheme comprising a pre-polymerization tank and a series of larger polymerization tanks. The proposed scheme allows the continuous operation of the process even when the reactors are operated in batch mode. Particularly, when the reacting slurry is transferred to the next vessel, the cleaning and coating steps can be performed in the previous vessel, diminishing the overall shut down time of the plant. Additionally, hydrocyclones are used to separate the components of the slurry that flow from the main polymerization tanks. Particularly, the authors reported significant reduction of water consumption (from 3-4 to 1.5-2.5 tons of water per ton of PVC) and increase of productivity (from 43 to 65 tons of PVC per day) in the proposed process.

Hong et al.<sup>[40]</sup> (from Yibin Tianyuan Group Co, CN) disclosed a method to perform the continuous production of PVC resins using microreactors. The proposed system comprises three reacting zones, which are designed to guarantee the achievement of a specified monomer conversion level. In order to maintain the reaction temperature at the desired value in each individual zone, the reaction temperature control should be performed independently for each reacting zone.

Based on the previous paragraphs, it becomes very clear that few processes have been claimed for the continuous manufacture of PVC powders produced in aqueous suspensions and that this does not reflect the much higher interest in developing continuous polymerization processes and suspension polymerization technologies. The few patents available in the field reveal that the authors acknowledge difficulties to control the residual monomer contents, the particle size distributions, and the incrustation of polymer on the internals and reactor walls. This can be related to the intrinsic characteristics of the VCM polymerization reactions (such as the heterogeneous nature of suspended droplets)<sup>[41]</sup> and the very polar nature of the PVC molecular structure, which facilitate the interaction with other materials and compounds (also facilitating sticking to metal surfaces and particle agglomeration)<sup>[42]</sup>, as discussed in the following sections. Besides, patents normally proposed processes that comprise a number of different reactors arranged in series in order to narrow the residence time distribution and allow the better control of the final particle size distributions, implicitly acknowledging that this is indeed a fundamental problem in the analyzed field. Unfortunately, this can also lead to additional internal contact areas and incrustation problems.

## 4.2 Initial search from scientific papers

After Search 1, 249 documents were found after removing non-relevant works. It can be seen in Figure 9 that publications on the subject became more frequently in 1976. The largest number of publications (20 papers) occurred in 2009, even though no trend or concentration of publications by a specific research group was identified. It is interesting to observe that these numbers are similar to the ones observed for patents, which is rare and probably due to regulatory constraints regarding handling of the VCM monomer in academic research environments<sup>[43,44]</sup>. Figure 10 shows the network visualization map for keywords used in papers for Search 1 and its respective references. As expected, "PVC" was



**Figure 9.** Annual production of scientific papers as found in Search 1.



Allsopp<sup>[54]</sup>, Hjertberg and Sörvik<sup>[58]</sup>, and Xie et al.<sup>[59]</sup> were not included in Search 1. Starnes<sup>[60]</sup> reported a review about thermal degradation of PVC. Particularly, no significant trend or concentration of publications could be detected in a particular research group. It is also worth noting that most analyzed publications evaluated modifications of the reaction formulation and process conditions for improvement of the process operation<sup>[61-63]</sup> and investigated the effects of different comonomers on the final properties of the obtained products<sup>[64,65]</sup>. Therefore, the scopes of the academic investigations were very different from the scopes of the patent literature, concentrated on the development of new processes, reactors, and products and particularly on the narrowing of particle size distributions and reduction of polymer fouling on internal reactor surfaces.

Table 3 shows the ranking of institutions according to the number of publications in the field. According to Table 3, the Zhejiang University (China) is the institution that publishes papers more frequently in the field, following the trend already observed for China in patents. Isfahan University of Technology (Iran) also appears as an important center of research in quantity of papers.

Usually, the number of papers for a given topic in the field of polymerization processes is much higher than the number of patents. However, this is not what is observed for PVC, given the difficulties imposed for use of VCM in universities due to its carcinogenic and explosive character<sup>[33]</sup>. Particularly, 318 papers were found after Search 2. However, when these papers were analyzed, it was observed that few in fact regarded continuous suspension polymerization processes. This occurred because of the constant use of the term “continuous” in other contexts within the publications, “deceiving” the search engine. When analyzing the titles of all downloaded papers, only 17 of the publications were indeed related to continuous suspension polymerization processes. Among these papers, only 9 of them described experimental studies<sup>[66-74]</sup>.

Liu et al.<sup>[70]</sup>, Zourob et al.<sup>[74]</sup>, Sen et al.<sup>[72]</sup>, Wang et al.<sup>[73]</sup>, and Bally et al.<sup>[67]</sup> investigated the use of microreactors to perform suspension polymerizations, whereas Lobry et al.<sup>[71]</sup> investigated the use of continuous oscillatory baffled reactors (COBR)<sup>[75,76]</sup> to produce suspension polymer powders. Even though Lobry et al.<sup>[71]</sup> mentioned the production of poly(vinyl chloride) in their work, the study was performed on vinyl acetate polymerization instead. Other works published by Pinto<sup>[77,78]</sup>, Hatate et al.<sup>[79]</sup>, Galkin et al.<sup>[80]</sup>, Galkin et al.<sup>[81]</sup>, and Kim et al.<sup>[82]</sup> were based on numerical investigation, simulation or CFD studies. The few academic works related to continuous suspension polymerization processes can be justified by the high operational costs of these reactions, since reagents must be used continuously, by the long periods of reaction needed to perform meaningful experimental analyses and attain steady-state operation conditions, and by the technological difficulties related to development of fouling on reactor internals, which still constitutes a significant unsolved technological problem in this field.

After Search 2, it becomes possible to conclude that the number of publications in the field of continuous suspension VCM polymerizations is very small. This is reinforced by results obtained after Search 3, which detected 22 papers

**Table 2.** Ranking of the most cited works of Search 1 for articles with 20 or more citations.

Ranking	Reference	Citations
1	Xie et al. <sup>[20]</sup>	39
2	Smallwood <sup>[45]</sup>	38
3	Saeki and Emura <sup>[26]</sup>	36
4	Kiparissides et al. <sup>[18]</sup>	31
5	Cebollada et al. <sup>[53]</sup>	29
6	Allsopp <sup>[54]</sup>	28
7	Davidson and Witenhafer <sup>[55]</sup>	27
8	Starnes et al. <sup>[56]</sup>	25
8	Abdelalim and Hamielec <sup>[57]</sup>	25
9	Hjertberg and Sörvik <sup>[58]</sup>	21
10	Xie et al. <sup>[59]</sup>	20
10	Starnes <sup>[60]</sup>	20

**Table 3.** Distribution of scientific papers by institutions as detected in Search 1.

Ranking	Institutions	Documents
1	Zhejiang University - CN	19
2	Isfahan University of Technology - IR	14
3	Aristotle University of Thessaloniki - GR	10
3	Loughborough University - GB	10
3	Israel Institute of Technology - IL	10
4	Ghent University - BE	9
4	University of Coimbra - PT	9
5	Federal University of Rio de Janeiro - BR	7
5	CIRES - PT	7
6	Braskem - BR	6
7	MacMaster University - CA	5
7	Slovak University of Technology in Bratislava - SK	5

that were not related to continuous polymerization processes at all. Apparently, only 2 papers dedicated to numerical investigations analyzed the nature of continuous suspension VCM polymerization processes<sup>[77,78]</sup>, emphasizing that these systems may present complex dynamics and multiple steady states. Although the published papers by Bodoc et al.<sup>[83]</sup> and Castor<sup>[64,84]</sup> were not listed in both Search 2 and Search 3, they are listed in Search 1 and investigated VCM polymerization in microreactors. Additionally, the authors were not listed because did not use “continuous” and “suspension” together either in title, abstract or keywords. However, it is important to highlight those works because of their scientific relevance in the polymerization field when dealing with VCM in microreactors.

Based on the obtained results, it can be said that research institutes and universities have contributed mainly with the development of kinetic mechanisms and process models for VCM suspension polymerizations, providing very limited support for development of continuous processes. Although this gap can be understood by the reasons already presented, this disconnection between the research carried out in industrial and academic environments can possibly

explain why significant breakthroughs have been relatively scarce in this field.

### 4.3 Types of processes from patents

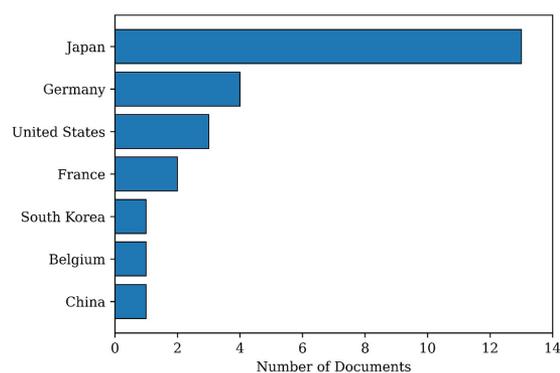
The search carried out for solution polymerizations resulted in 48 documents, although only 28 of them were indeed related to VCM solution polymerization processes. Due to the small number of documents, it is not possible to observe trends related to the use of this polymerization procedure. Among the main subjects of these documents, modification of PVC formulations and prevention of fouling stand out. Modifications of PVC formulations are certainly powered by market demands, while prevention of fouling constitutes a still unsolved industrial problem that prevents the development of continuous operations and encourages innovative applications.

As shown in Figure 12, Japan is the country where most patents were filed as priority, mainly because Japanese companies also lead the number of deposits. As the solution VCM polymerization process is not commercially important and there is little demand for solution PVC materials, the number of patents on the subject is also small. As pointed out previously, the small interest in solution polymerization processes is due mainly to the high downstream costs of solvent removal and purification.

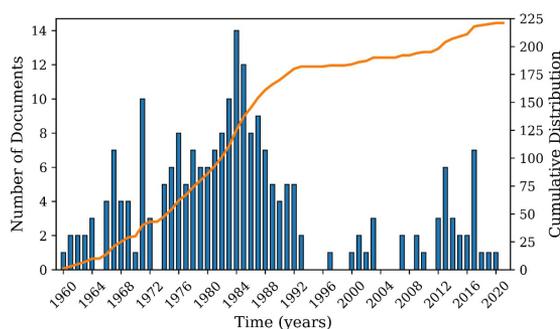
The search carried out for bulk polymerizations resulted in 221 documents. It can be seen in Figure 13 that the same production profile observed after Search 1, as illustrated in Figure 3, could be observed for patents related to VCM bulk polymerization systems. The reduction of patent production after 1984 can be justified by the maturity of the technology, but also to investigations related to VCM toxicity and consequent enforced regulations<sup>[44]</sup>. Particularly, VCM bulk polymerizations can generate very fine polymer powders, which can lead to processing problems and be harmful to health by inhalation during handling<sup>[33]</sup>. It must also be emphasized that it is difficult to manipulate the morphological features of bulk PVC powders, which can also explain why Figure 13 clearly shows the significant reduction of interest in this technology. Nevertheless, Table 4 shows a list of the most active patent depositors in the last 20 years in this field. Although LG Chemical (South Korea) has led the number of deposits in recent years, most of the patents have been filed by Chinese companies, following the demands of the Chinese construction market.

Regarding the technologies covered by the patents deposited in the field, strategies to reduce the production of fines, modifications of the resin formulations and manipulation of process variables (agitation speed, for example) to optimize the process performance stand out<sup>[85,86]</sup>. The reduction of

fines constitutes a recurring concern in patents related to VCM bulk polymerization processes because the final polymer particles, if measures are not taken, can be very small, causing processing operation problems and health risks to those who handle the powder<sup>[23]</sup>. For this reason, the use of dispersants, such as  $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ , has been reported to increase the average particle size of the resin<sup>[85]</sup>. Nevertheless, in the last 20 years only one patent reported the existence of problems related to fouling in bulk polymerization processes of VCM. In this case, Hong et al.<sup>[87]</sup> (patent from Yibin Tianyuan Group Co., CN) recommended the use of nitric acid to reduce the pH of the reaction medium and avoid the formation of polymer aggregates and fouling. According to the authors, nitric acid acts as a passivator on the internal surfaces of stainless steel reactors, reducing the adhesion of polymer material onto the metal surfaces. Apparently, this patent exerted little influence on other alternative PVC technologies.



**Figure 12.** Distribution per country of patents related to solution polymerizations of VCM.



**Figure 13.** Annual production of patents related to bulk polymerizations of VCM.

**Table 4.** Distribution of patents in the 6 most productive institutions in the field of bulk polymerization of VCM in the period 2001-2021.

Ranking	Institutions	Documents	Percentages
1	LG Chemical (South Korea)	6	16.2%
2	Yibin Tianyuan Group (China)	5	13.5%
3	Chengdu Sino-Metal Tools (China)	2	5.4%
4	Starna Group (Italy)	1	6.3%
5	Wenzhou University (China)	1	6.3%
6	Sabic (Saudi Arabia)	1	6.3%

502 documents were found for emulsion VCM polymerizations. It can be seen in Figure 14 that the interest in PVC emulsion technologies grew fast in the 1970s on, remained approximately constant until the mid-2000s and apparently diminished after that. This seems to be connected to the technological maturity achieved by emulsion PVC processes, as the main trends of the PVC field discussed previously and shown in Figure 3 cannot be observed in this case. It is important to highlight that PVC emulsions are used widely to manufacture plastisol and pastes for coating and paints<sup>[88]</sup>. As a matter of fact, in the past 20 years, 75 patents have been filed on this particular subject.

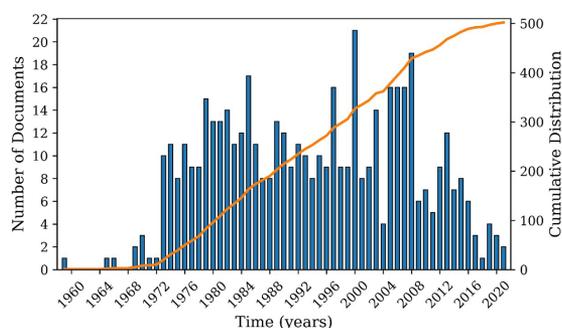
Table 5 reports the most productive patent depositor companies in the last 20 years in the field of VCM emulsion polymerization. As one can see, LG Chemical leads the list with large advantage over its competitors due to the special corporate attention to PVC plastisol and pastes markets. Besides, Asian companies have been dominating the innovative activity in this field, being responsible for about 75% of patent deposits in the last 20 years, which is aligned with the growing demand for PVC in Asia.

Regarding the main technological trends of deposited patents, there is significant concentration on development of new products, either through copolymerization with other monomers or modification of the reaction formulation to obtain differentiated products. In many cases, although patents are not focused on the process itself, claims also include innovative aspects of the reaction process associated specifically with the proposed formulation changes. However, relatively few novelties regard the reaction process or the reaction vessels exactly. For instance, Kazuhiro and Tadashi<sup>[89]</sup> (from Shin-Etsu Chemical, JP) developed a procedure to

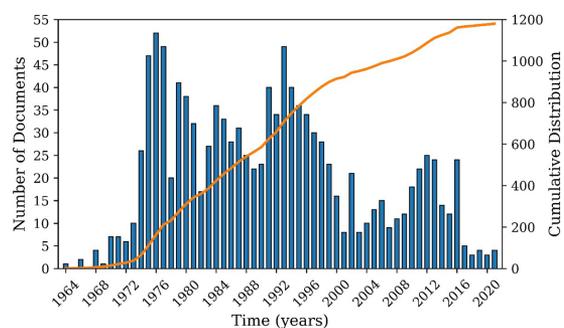
prevent the adhesion of polymer material to the internal surfaces of the reaction vessel, based on the application of methanolic solutions of aromatic compounds to reactor walls before the polymerization step. Toshiaki et al.<sup>[90]</sup> (from Kanegafushi Chemical, nowadays Kaneka Corporation, JP) reported the development of a continuous process for manufacture of copolymers of acrylic monomers and VCM. In most of these patents, reactions are performed in agitated tank reactors (including tubular reactors equipped with multiple effect mixers) or tubular reactors (including pulsed sieve tubular reactors).

The use of anti-adherent agents is not new in polymerization processes, since it has been known for a long time that polymers encrust on equipment and reactor walls. Therefore, many efforts have already been made in the past to overcome this problem, since this may allow the significant reduction of reactor shutdowns for cleaning. As a result, it should be expected that many companies would introduce new anti-adherent products (and file the respective patents) that promise to allow the maximization of process productivity through minimization of reactor shutdowns for cleaning and maintenance at the industrial plant.

1180 patents were found regarding VCM suspension polymerization processes. As shown in Figure 15, the number of patent deposits related to VCM suspension polymerizations is much higher than those related to the other VCM polymerization processes, since this is the most important commercial process used for manufacture of PVC. Particularly, the same trends presented in Figure 3 can be identified in Figure 15, as suspension processes determine the main trends of the PVC commercial markets. Moreover, 224 patents have been identified in the field over the past



**Figure 14.** Annual production of patents related to emulsion polymerizations of VCM.



**Figure 15.** Annual production of patents related to suspension polymerizations of VCM.

**Table 5.** Distribution of patents in the 7 most productive institutions in the field of emulsion polymerization of VCM in the period 2001-2021.

Ranking	Institutions	Documents	Percentages
1	LG Chemical (KR)	19	10.9%
2	Kaneka (JP)	6	3.4%
3	Tosoh (JP)	5	2.9%
4	Sekisui Chemical (JP)	3	2.9%
5	Mitsubishi Chemical (JP)	3	2.9%
6	BASF (DE)	3	2.9%
7	Arkema (FR)	3	2.9%

20 years, showing the continuous interest in development of technologies in the field, although the reduction of patent deposits in the last decade is obvious (Figure 15) and probably reflects the technological maturity of the area. As observed in the vinyl chloride emulsion polymerization search, Table 6 shows that the LG Chemical (South Korea) is also the leader of patent deposits related to suspension polymerizations of VCM, being responsible for 25% (57 patents) of the deposits in the past 20 years, well ahead of the second largest patent depositor, the Kaneka Corporation (Japan), which filed 22 patents in the same period. As a matter of fact, Asian companies were responsible for 83% of the patent deposits in this field in the last 20 years, so that all the first 11 most productive patent producers in the analyzed area are Asian. This number confirms the enormous interest and demand of the Asian market for PVC, reflecting the demand generated by the growing Chinese construction business, but also reflecting the fact that Asia has become a major worldwide provider of PVC for economic and regulatory reasons.

Regarding the technological trends, prevention of fouling constitutes the most explored subject for technological development (22 patents) in the last 20 years for VCM suspension polymerization processes (for example, Beyong-Guk et al.<sup>[91]</sup>, from Denki Kagaku, JP; Takahiro et al.<sup>[92]</sup>, from JNC, JP), followed by modification of the suspending agent (21 patents) (for example, Jun et al.<sup>[93]</sup>, from LG Chemical, KR; Paul et al.<sup>[94]</sup>, from Hanwha Chemical, KR), which clearly indicates that control of particle agglomeration and of particle morphological features constitute the main process bottleneck and the main concern for innovative activity. As the suspension polymerization process is the most important commercially, the most flexible for control of particle morphology and leads to still unsolved fouling problems, it is easy to understand the large number of patents that are related to these subjects in the field. It is also important to highlight that most technologies proposed to prevent fouling describe addition of new anti-adherent agents and development of the respective application procedures, so that these patents do not propose revolutionary technologies to combat the fouling problem. Moreover, the search for new PVC-based commercial grades and materials is reflected by the relatively high number of patents related to new copolymer materials and copolymerization processes (18 patents).

#### 4.4 Types of processes from scientific papers

Firstly, searches performed for all types of VCM polymerization processes did not detect any investigation associated with fouling prevention technologies. This clearly

shows from the very beginning that the scopes of investigations performed in academic and industrial environments about VCM polymerizations can be quite different. Particularly, the apparent lack of interest of the academic environment on studying the fouling problem, the fouling mechanism and respective modeling possibly explains why advances take place so slowly in the field.

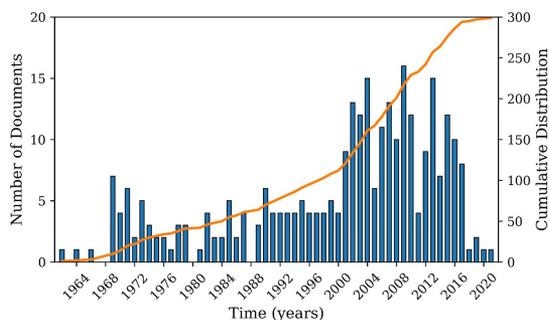
When the search was constrained to articles on solution VCM polymerizations, 249 articles could be found. However, only 4 of these documents really investigated aspects of the VCM polymerization process performed in solution in the last 20 years<sup>[95-98]</sup>, as the large majority of the available manuscripts make use of the solution technology to manufacture materials with distinct properties, through modification of feed formulation, copolymerization with other comonomers or appropriate control of the molar mass distributions of the final product. This probably reflects the fact that it is much easier and comfortable to produce polymer materials in small lab scale reactors in solution. In these cases, the process should be regarded as a tool that is used to produce the polymer material, which constitutes the actual target of the investigation. Besides, the large fraction of papers that make use of solution processes for manufacture of PVC does not reflect the commercial interest in this field, as shown in the previous section.

The search for articles regarding VCM bulk polymerization processes resulted in 49 hits, although only 4 of these articles were indeed focused on the investigation of aspects of VCM bulk polymerization processes<sup>[99-102]</sup>. As in the previous case, these studies focus on minor improvements on the process operation rather than on breakthrough technologies. Besides, the bulk technology has normally been used mostly as benchmark for modeling and simulation studies<sup>[103]</sup>, due to safety and regulatory constraints regarding the use of VCM in universities and research institutes, which inhibit the development of experimental studies in these institutions.

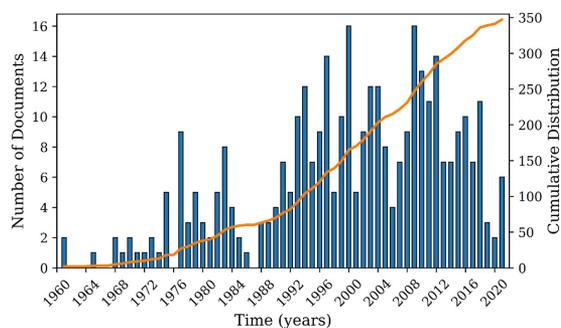
The search for articles related to VCM emulsion polymerization processes resulted in 299 hits. As Figure 16 illustrates, there was a continuous and slow increase of interest in the subject over the years, although apparently the number of papers related to VCM emulsion polymerizations diminished dramatically in the last decade, reflecting somehow the same behavior observed in Figure 14 for patents. The slow increase of interest can be explained by the easier handling of dispersed reaction media in the laboratory, due to combination of reduced amounts of monomer and safer operation conditions and to the fast development of nanotechnology, given the characteristic

**Table 6.** Distribution of patents in the 6 most productive institutions in the field of suspension polymerization of VCM in the period 2001-2021.

Ranking	Institutions	Documents	Percentages
1	LG Chemical (South Korea)	57	30.8%
2	Kaneka (Japan)	11	5.9%
3	Shanghai Chlor-Alkali Chemical (China)	7	3.8%
4	Shin-Etsu (Japan)	7	3.8%
5	Hanwha Chemical (Japan)	6	3.2%
6	Tianchen Chemical (China)	6	3.2%



**Figure 16.** Annual production of articles related to emulsion polymerizations of VCM.



**Figure 17.** Annual production of articles related to suspension polymerizations of VCM.

nanosizes of emulsified polymer particles. As a matter of fact, most of the scientific papers related to PVC emulsions regard the manufacture of blends and processing of PVC pastes<sup>[104-107]</sup>, not polymerization processes. Table 7 shows the most productive institutions of scientific articles regarding VCM emulsion polymerization processes in the last 20 years. Works from Hebei University of Technology are the leading in this list, with 22 papers in the analyzed period. It must also be observed that the main trends in the field, as observed from scientific papers, involve the preparation of new composites<sup>[108,109]</sup> and copolymers<sup>[110,111]</sup>. As also observed previously, many investigations regard theoretical and simulation studies<sup>[112-115]</sup>, again, due to the difficulty of using VCM in the universities.

347 papers were found during the search for papers on VCM suspension polymerization processes, as shown in Figure 17. As in the previous cases, the number of publications in this field has decreased over the last decade, which can reflect the lower innovative activity of companies, as also described in Figure 15. Moreover, as observed previously, many papers were targeted on the product properties, not exactly on the polymerization process. However, after proper filtering of downloaded manuscripts, 121 papers were found to investigate VCM suspension polymerization processes in the analyzed period, a much larger number of articles than observed before and reflecting the commercial importance of VCM suspension polymerization systems. Table 8 shows the most productive institutions of scientific articles regarding VCM suspension polymerization processes in the last 20 years. Works from Zhejiang University of Technology are the leading in this list, with 19 papers in the analyzed period. Observing the subjects of the downloaded papers, the main scientific trends in the area regard the modification of PVC and production of new materials with distinct characteristics, as also discussed previously, particularly through production of composites and nanocomposites<sup>[116-118]</sup> and copolymers<sup>[104,119,120]</sup>. Besides, as also observed before, there is a relatively large number of papers dedicated to development of process models<sup>[28,104,119-123]</sup>, with more recent concentration on CFD (computational fluid dynamics) simulations performed to understand the effects of reactor design and reactor internals on mixing patterns and evolution of particle size distributions<sup>[124-127]</sup>.

**Table 7.** Publication frequencies of the most productive authors in the field of emulsion polymerization of VCM in the period 2001-2021.

Ranking	Institutions	Articles
1	Hebei University of Technology - CN	22
2	Changchun University of Technology - CN	21
3	Chinese Academy of Sciences - CN	11

**Table 8.** Publication frequencies of the most productive authors in the field of suspension polymerization of VCM in the period 1998-2021.

Ranking	Institutions	Articles
1	Zhejiang University of Technology - CN	19
2	Isfahan University of Technology - IR	15
3	Ghent University - BE	10
4	Federal University of Rio de Janeiro - BR	9
5	Loughborough University - GB	8
5	University of Pannonia - HU	8

#### 4.5 Additional remarks

According to the previous analyses, the field of VCM polymerization processes is currently characterized by declining innovative activity, as determined for both the technological (through patents) and academic (through scientific publications) literature. This can be the result of the technological maturity of the area, as the current processes have remained essentially the same since the 1980s and innovative activities have been of incremental nature, although can also be due to increasing regulatory constraints related to the potential health risks posed by VCM handling and using. This also explains why the patent literature is more abundant than the academic literature in the field, which is indeed rare, as handling of VCM is limited in most universities and research institutes of the world. Besides, the academic literature is largely concentrated on development of new PVC products and simulation studies, and not on development of VCM polymerization processes supported by experiments. Therefore, PVC manufacturers face the important challenge of providing the breakthroughs

that the field demands, although receiving limited support from universities and research institutes, which can also explain the recent decline of innovative activities in the field. Therefore, it seems correct to say that the academic interest in PVC polymerization technologies should be stimulated by companies that operate in this field. However, in order to overcome the increasing regulatory constraints, companies should find opportunities for joint development of academic research inside the industrial facilities, somehow inverting the usual human flow direction and opening space for academic researchers to remain in the industrial labs for at least part of their working time.

Among the most expected breakthroughs, two subjects must receive particular attention: development of continuous VCM suspension polymerization processes and prevention of polymer fouling during suspension polymerization operations (which are indeed interconnected, as fouling prevents the continuous process operation). Not surprisingly, these two subjects have not constituted research topics in academic environments, as both depend strongly on the support of experimental data. Besides, innovative activities in these areas have been quite conservative, in the sense that they have been concentrated on the analysis of anti-fouling agents. Despite that, recently deposited patents indicate that PVC manufacturers are still searching for more advanced solutions that can be combined with new reactor designs. For instance, the continuous oscillatory baffled reactors (COBR)<sup>[71]</sup> and recent microreactor technologies<sup>[40]</sup> can provide the future breakthroughs that may eventually allow the continuous manufacture of PVC, as they can simultaneously prevent fouling through the inherent self-cleaning characteristics of the turbulent oscillatory flow in COBR's and by avoiding the impact of sticky polymer droplets against reactor internals in microreactors.

## 5 Conclusions

Bibliographic searches focused on VCM (vinyl chloride monomer) polymerizations indicated that innovative activity is declining in the field of VCM polymerization processes. Possible explanations involve the regulatory constraints related to VCM handling and utilization, the maturity of the technology and existence of significant unsolved technological problems, such as the fouling caused by polymer sticking to internal reactor surfaces and, consequently, the possibility to operate the VCM suspension polymerization reactors continuously. Due to the regulatory constraints, the number of patents available in the technological literature is higher than the number of scientific papers published in scientific journals, which is rare.

Because of the commercial importance of PVC emulsions, pastes and powders, particularly for the construction business, VCM emulsion and suspension polymerization processes are the most studied ones, especially the last ones. However, most studies have been concentrated on the development of new PVC-based formulations, blends, composites and copolymers, not on development of manufacture processes. Therefore, additional research is needed to provide solutions to prevent polymer fouling during suspension polymerization operations and allow the continuous operation of VCM suspension polymerization processes.

As observed in the bibliographic search, these two subjects have not constituted research topics in academic environments, as both depend strongly on the support of experimental data and regulatory constraints inhibit experimental academic activities in this field. This creates a disconnection between the research projects conducted in industrial and academic environments that can possibly explain the slow pace of innovative activities in the field and should stimulate companies to develop cooperative projects with research institutes and universities in the industrial environments.

Finally, future technological breakthroughs should provide support for migration from batch to continuous PVC suspension polymerization processes<sup>[40,71]</sup>. Although this trajectory remains limited by unsolved fouling problems, innovative reactor designs can simultaneously provide means to minimize fouling onto reactor internals and to allow the operation in continuous mode. Some innovative reactor designs include the continuous oscillatory baffled reactors (COBR) and some microreactor technologies, which can prevent fouling through the inherent self-cleaning characteristics of the turbulent oscillatory flow in COBR's and by avoiding the impact of sticky polymer droplets against reactor internals in microreactors.

## 6. Author's Contribution

- **Conceptualization** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Data curation** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Formal analysis** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Funding acquisition** – José Carlos Pinto.
- **Investigation** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Methodology** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Project administration** – José Carlos Pinto.
- **Resources** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Software** – NA.
- **Supervision** – José Carlos Pinto.
- **Validation** – NA.
- **Visualization** – NA.
- **Writing – original draft** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.
- **Writing – review & editing** – Rafael Lima; Jonildo Silva; Mateus Vasconcelos; Carlos Alberto Castor Junior; José Carlos Pinto.

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