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# Application of expandable polymeric microspheres in the preparation of materials: A review of the literature

## Aplicación de microesferas poliméricas expandibles en la elaboración de materiales: Una revisión de la literatura

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## Summary

The strategic management of scientific-technological information is increasingly important to innovate in the development of new products and processes. Research work in different areas such as materials science, in conjunction with industry, is the perfect formula to discover a product, improve an existing one and find alternative applications. This article presents a review of the literature about the main characteristics and trends in the use of expandable polymer microspheres, including applications derived from both completed studies and research lines in development. Some outstanding applications are: the superficial modification of some types of materials such as leather, thermal insulation, manufacture of parts for automobiles and manufacture of maxillofacial prostheses. Among the potential applications that are worth highlighting are: the manufacture of materials with acoustic insulation and as a component in materials, such as elastomers for obtaining lightweight and comfortable soles.

Keywords: Polymeric materials; Expancel; rubber compound; soles and lightness.

## Introduction

Every day, new materials venture into the market, thanks to the results of scientific work that converge with industrial needs for a specific application. The expandable polymeric microspheres (MPE), produced by the Dutch multinational Akzo Nobel, under the trade name Expancel® (Minerals, n.d.) are an example of this. Currently, they are applied in the development of different materials, thanks to certain properties, among which, the most important are: low density, acoustic insulation capacity, resistance to corrosion and ability to modify surfaces (Rangari, Jeelani, Zhou & Jeelani , 2008). The growing interest to improve the performance of the MPE and find other uses, has strengthened the studies related to their characteristics and processing (Osorio & Londoño, 2011). However, when conducting a thorough review in the Scopus databases, it was found that published research on MPEs, to date, is significantly few. Conclusion which was reached when comparing publications related to other types of microspheres such as glass.

That is to say, it can be intuited that the field of application of the MPE for the development of new materials is still to be discovered. In the case of elastomeric materials there are few studies that include the use of MPE, among them it has been found that they have been used for the manufacture of rims and maxillofacial prostheses. In these products, the MPEs reduced the amount of raw material, decreased the weight, lowered the cost and reduced the energy consumption during processing (Hatamleh, Polyzois, Nuseir, Hatamleh & Alnazzawi, 2015, Liu et al., 2013; Mori & Hotaka, 2003; Yamaguchi & Amino, 2003).

The footwear industry can be an important sector for the use of the MPE as a raw material. This is intuited given the characteristics and functionality of the MPE and also by the fact that existing companies in the sector that are highly competitive, invest more and more in the innovation of their products to meet the demand of more demanding users. For example, lightness is a characteristic that is obtained in a composite material due to the expansion of these microspheres in it. If this material is applied on soles, it would help to obtain a lighter and healthier shoe for the user.

Currently, the footwear industry is using various types of polymeric materials for the manufacture of soles, among which stand out: poly (vinyl chloride) (PVC), poly (ethylene-vinylacetate) (EVA), polyurethane (PU), thermoplastic polyurethane (TPU) and natural rubber (NR, for its acronym in English) (Bruckner, Odenwald, Schwanitz, Heidenfelder & Milani, 2010). With the exception of NR, both EVA, PVC and PU are synthetic polymers and all have been widely studied (Kim, Park, Chowdhury & Kim, 2004, Lopes, Ferreira, Russo & Dias, 2015).

In 1868, rubber began to be used as material for soles for sports shoes, and already in the twentieth century, with the development of new varieties of rubber and additives to improve their properties, their use in soles increased significantly.

In the 1940s and 1960s, *Puma* and *Adidas*, in Europe, and *Tiger* in Japan began to implement biomechanical and medical criteria for the design and manufacture of their shoes. Approach adopted by other companies such as *Nike*, *Converse* and *Brooks* in the 1970s (Galarza & González, 2014, Palopoli, 2014). This undoubtedly affected the progress of certain lines of research, mainly in materials science, design and biomechanics.

The panorama described allows us to glimpse the opportunity to take advantage of new materials, as it is the case of the MPE, for the processing of various elastomers and in particular of the rubbers used in the footwear industry, and thus have a new alternative for this type of applications especially because the concept of lightness is highly influential for the development of sports and women's footwear.

Therefore, the development of new rubber-based materials and MPE is an important topic of study which it has not yet been sufficiently explored and whose results would lead to an alternative application for MSEs.

In order to develop this type of material, first of all it is essential to review the literature and identify the current scientific and technological applications of the MPE. Thus, the theoretical knowledge about the characteristics and functionality of the MPE would be obtained, as well as the viability of its insertion in elastomeric materials. For this reason, this paper presents a review of the literature on rubber, the additives used in the formulations of this material, on the MPE and particularly on the applications of these microspheres.

## Generalities about rubber

Elastomers or rubbers are a type of polymer material of great interest because they have very useful physical, chemical and mechanical properties. Among them are mentioned: its high elasticity, its high resistance to the environment and high temperatures, its electric insulation capacity and its relatively low density. It can be obtained naturally or synthetically; Synthetic rubbers are obtained by means of chemical reactions, where the same monomer or several monomers participate, and among them stand out: styrene butadiene (SBR), polybutadiene (BR), ethylene propylene diene (EPDM), chloroprene or neoprene (CR ) and acrylonitrile butadiene (NBR). As for natural rubber, it is obtained after the coagulation of the latex extracted from the tree of the species Hevea brasiliensis, native to the Amazon region (Martínez, 2005, Osorio, 2013, Urrego, 2014).

With the discovery of the process of vulcanization in 1839 by Charles Goodyear, the materials produced in rubber have increased their participation substantially in the world market, to the point of being today of high utility in different fields or sectors such as the automobile, seals, profiles, clothing and footwear (Castaño, 2012, Isayev, 2013, Peláez, Velásquez, & Giraldo, 2014), these being some of the most relevant.

In 2015 it was reported that world rubber production oscillated close to 12,196 million tons and some estimates predicted that by 2016 production would increase reaching figures close to 12,255 million tons (Industriall Global Union, 2013), Ministry of Agriculture, 2016. The demand for this material has presented a substantial increase in the recent decades, only in the last 13 years has consumption increased on average by 4% per year (De Carvalho et al., 2013; Malaysia, 2015). For this reason, the advances that the rubber industry has reached in recent years have been reflected in the diversity of applications that are currently requested for this type of material.

## Additives used in the formulation of rubber compounds

The development that elastomeric materials have presented is largely due to its formulation, in which substances are added in a certain proportion to the base material or matrix, to achieve a specific objective (Peña, 2007, Vargas, 2004). Generally, this seeks to improve certain characteristics of the base material, such as performance during operation. As a result, its fields of application are expanded and its benefits are improved (Osorio & Londoño, 2011).

The additives used in the formulation of rubbers are generally referred to as their functionality as: fillers or fillers, plasticizers, protective agents, activators, accelerators and vulcanizers, these being some of the most relevant.

The density and proportion of the additives will determine the final density of the rubber compound. Thus, for example, carbon black, which is denser than rubber, will increase the density of the formed composite, the more amount of carbon black is added thereto, on the contrary oils or plasticizers, whose density is lower than that of rubber, will decrease the density of the compound as its content increases (Peña, 2007, Vargas, 2004).

Some substances from natural sources are used as additives for rubber compounds, such as natural fibers (Jacob, Thomas, & Varughese, 2004; Zhou, Fan, Chen, & Zhuang, 2015) and palm ashes (Ooi, Ismail, & Bakar, 2013, 2014). Other nanometric additives, such as silica, nanoclays and carbon nanotubes are also investigated (Alipour, Naderi & Ghoreishy, 2013; George, Rajan, Aprem, Thomas & Kim, 2016; Park et al., 2013; Yánez Bolívar , 2007; Ziraki, Zebarjad & Hadianfard, 2016).

Currently, other additives that act as foaming agents are being used, of which a large number of references, brands and types already exist. These agents can be of the chemical or non-chemical type (Osorio & Londoño, 2011). In the first type, a chemical reaction occurs that generates a residual product, which can be gas, water or another particle. Therefore pores and bubbles are formed in the structure of the material containing the foaming agent, after the reaction occurs. If in the reaction there is release or absorption of heat, the chemical agents in turn can be of the exothermic or endothermic type, respectively (Osorio & Londoño, 2011). In the case of agents of the non-chemical type, no reaction occurs that causes some residual product.

Among the main characteristics that these agents provide to a material are: reduction of density, high resistance per unit of weight, greater thermal insulation, better qualities of absorption of energy or direct impact and reduction in costs by using less of the base material for the same volume (AkzoNobel, 2013; Barzegari, Yao, & Rodrigue, 2013; Osorio & Londoño, 2011).

As indicated in certain investigations (González, Álvarez García, & Abreu González, 2008, Ibarra, Posadas & Esteban-Martínez, 2004), foaming agents of the non-chemical type have already been used as additives for NR, silicone and BR .

MPEs are foaming agents of the non-chemical type, which have been used as additives for rubber, as low density fillers. (AkzoNobel, 2014a, Meguriya & Tomizawa, 2001, Wilson et al., 2007). For example, the addition of MPE in silicone allowed obtaining a material that provided higher performance in maxillofacial prostheses (Hatamleh et al., 2015, Liu et al., 2013) and also in NR and BR rims (Mori & Hotaka, 2003). ; Yamaguchi & Amino, 2003).

Despite the existing variety of additives for rubber compounds, research continues to develop new, and achieve other formulations that reduce costs, improve mechanical properties, integrate functions of several pieces into one and decrease the density of the final composite (Osorio & Londoño, 2011).

## *Use of the MPE as an additive in different types of materials*

Within the variety of MPE used in the processing of different types of materials, it has been found that a type of non-chemical foaming agent of great use is the product of the Dutch multinational AkzoNobel, known as Expancel® (Ahmad, 2001, AkzoNobel, 2014b, 2014c, 2014d). This product are white microspheres, with a particle size of 10 to 40 µm (unexpanded), formed by a polymeric coating or base, which is generally polyacrylonitrile (PAN), EVA or in some cases poly (methyl methacrylate). (PMMA) (Everett, Matic, Harveyii & Kee, 1998; Soares & Nachtigall, 2013; Vaikhanksi & Nutt, 2003) and inside it contains a hydrocarbon in a liquid state, which under heat increases its pressure when it enters the gaseous state. Thus, the polymer cover is reduced and the particle expansion occurs, ie its volume increases (Andersson, Griss & Stemme, 2002, Lu, Broughton & Winfield, 2016, Tomalino & Bianchini, 1997). The temperature range for its expansion, in general, is between 80 and 240 ° C (AkzoNobel, 2013, Osorio & Londoño, 2011). It should be noted that there are several references of Expancel®, differentiated according to their process of obtaining and optimal working conditions (Banea, Silva, Carbas & Campilho, 2014, Lu et al., 2016, Osorio & Londoño, 2011, Scognamillo et al. 2014). For each of them, the temperature range and the final expansion diameter are different (Minerals, n.d.). For example, one type of MPE can have an expansion range between 80 and 190 ° C, and an increase in diameter corresponding to 4 times its initial diameter, as shown in Figure 1. (A) (Andersson et al. ., 2002), while for the references: 930-120, 951-120, 551-40, 820-40 and 051-40, the temperature ranges and the final expansion diameters are different, as indicated in the Figure 1 B).

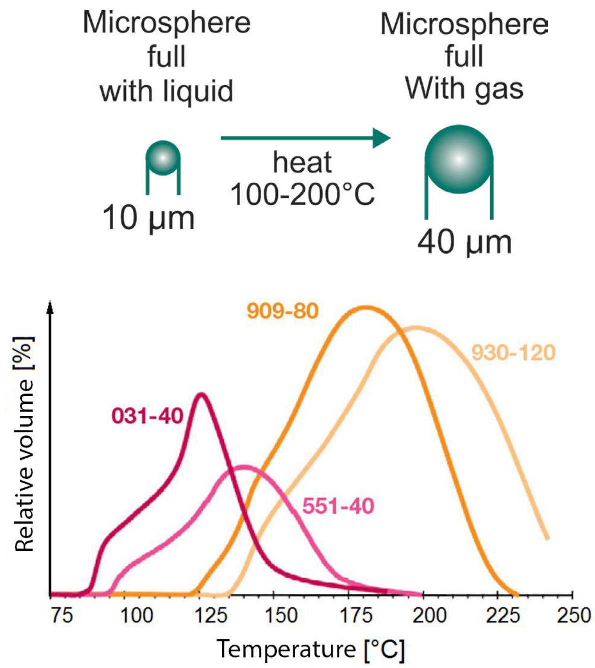


**Figure 1. (A)** Scheme of the expansion of the MPE (Andersson et al., 2002) and **(B)** Intervals of expansion of different types of MPE (Minerals, n.d.)

The MPE is a novel alternative as a foaming agent since it has been reported that used in a dosage of 3% by weight, it generates a reduction in weight of the material up to 38% in rotomolded plastic pieces (Osorio & Londoño, 2011). This type of effect is a great economic advantage for certain manufacturing companies, since they could use less raw material for the production of their products.

The MPEs have been used in injection, extrusion and rotational molding processes due to their easy handling and to obtain parts with 100% closed cell and controlled cell size, depending on the type of sphere used (Osorio & Londoño, 2011). Another material to which MPE has been added is cement mixtures (Aglan et al., 2009).

## *Applications of the MPE in the footwear industry*

The footwear industry is constantly searching for new materials and new technologies that minimize the negative impacts that their products generate on people's health (Ochoa, 2011). The most flexible and light footwear concepts are essential to achieve it.

The local market offers footwear with some special characteristics in terms of design and materials, other markets mainly of international character present new technologies for the manufacture of soles and insoles. Certain investigations have developed soles with expandable additives (Erb, Jin Kim & Grott, 2006). Likewise, the multinational AkzoNobel has reported the use of MPE in thermoplastic materials for soles (AkzoNobel, 2014b). That is, the investigations are evidence of the current tendency to incorporate foaming agents in materials used for shoe soles. This supports the possibility of conducting research to evaluate the addition of MPE in rubber, for soles of optimum quality, lighter and with good mechanical performance.

## Evolution of the MPE from its origin

búsqueda In addition to the bibliographic search that was carried out in different databases, a technological surveillance was carried out using the database with the largest number of abstracts and bibliographic references of known scientific literature: Scopus. This tool showed how research in the area of materials is constant and rapidly increasing. The search term initially used was "Expancel", because this is the registered trademark of the most used MPEs. As a result of the search, 31 related publications were found.

An analysis was made of the number of publications per year, the countries that have published research associated with the MPE and the areas of interest that have studied this type of material. Figure 2 shows the number of publications per year in subjects related to the MPE from the 80s to the year 2015. The year 2008 presented the largest number of writings referring to the MPE (Expancel®), with a total of 6 documents. While in the periods between 1981 to 1993 and 1995 to 2001 there were no publications. In 2015, only one publication was made.

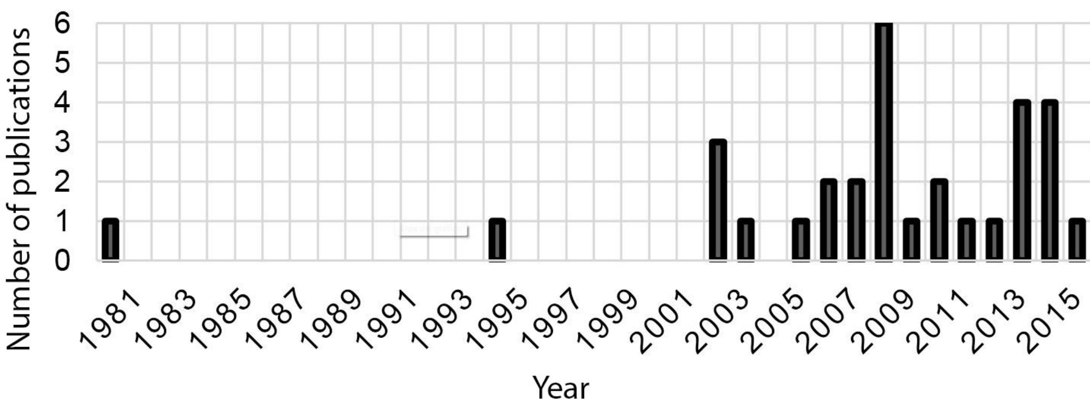


**Figure 2.** Documents per year on MPE in the world. Compiled from Scopus.

The first study on MPE dates back to 1981; Although they have been the subject of study by different authors, there are others that have not yet been addressed, such as the effect of the incorporation of MPEs into rubber matrices, their processability, mechanical behavior, among others. These are issues of a complexity of their own that require a holistic approach to their real development.

From the year 2001, the publication of studies on the MPE increased, thanks to the advance of the technology and with it the development of new equipment that allowed to study this type of materials and their behavior.

Although nowadays there are different types of microspheres in the market, among which the glass ones stand out because they have been more widely studied for diverse applications, the publication of studies on the MPEs has been intermittent. This situation could change, It has been mentioned that MPEs have characteristics that are of interest for certain industrial sectors and applications not yet explored, so that research on them may be increasing.

When identifying the country where the 31 documents were published, a total of 15 was obtained. Figure 3 shows the ranking of countries that are investigating, innovating and developing studies on the subject of the MPE. Although the number of publications on this subject is significantly lower than that of other types of materials, it is true that the difference in the number of publications between countries is relevant. It should be noted that the United States has a total of 10 publications, while Sweden has 4 publications, Canada and Japan 3, while China, Germany, Poland and Ukraine have 2 publications.

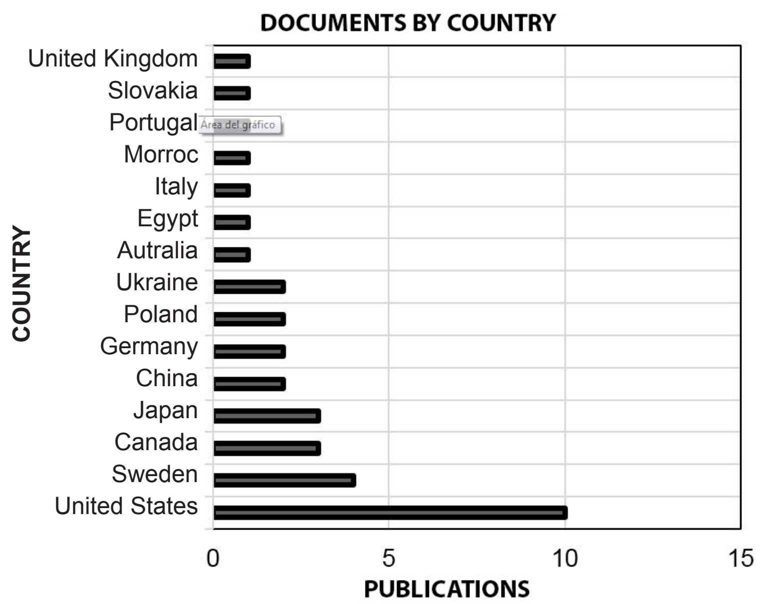


**Figure 3.** Documents by country on MPE. *Compiled from Scopus*

Another aspect that is vital to develop this comparison is the number of research groups and the number of researchers linked to them, related to the study of the MPE. In Colombia, the study of this type of material has been limited, there are few researchers and existing research groups, with lines of research on the MPE.

Finally, the 31 documents found were compared according to the search equation "Expancel", with the thematic area to which they belong. However, the initial comparison was made in 15 thematic areas, of which only 7 are of interest, due to the fields of application that are to be addressed.Table 1 presents the totality of documents by thematic área.

**Table 1.** Number of publications by thematic area. *Compiled by Scopus.*

| Documents by thematic area | Number of publications | Proportion over the total |
|---|---|---|
| Engineering | 17 | 32% |
| Material science | 16 | 30% |
| Biochemistry, genetics and molecular biology | 5 | 9% |
| Chemical engineering | 5 | 9% |
| Química | 4 | 8% |
| Física y Astronomía | 4 | 8% |
| Medicina | 2 | 4% |

## Conclusions

Technological surveillance in subjects related to the fields of action of a research group leads to the detection of alternatives with high application potential. This was the case of the expandable polymer microspheres (MPEs), which can be used in the research areas of SENA's Leather Design and Manufacturing Center. Therefore, a review of the literature was carried out with a view to establishing, in addition to technological surveillance, a state of the art on these types of products and thus identifying possible lines of research on the subject.

The review of the literature made it possible to identify that there are relatively few studies conducted on the MPE, and that most of the publications on the subject come from the science and engineering of the materials, and in lesser quantity in areas such as biochemistry, engineering chemistry, physics and medicine. It is concluded that MPEs are used in various applications, but it is pertinent to advance in their study with a view to finding new fields of action.

One of the most feasible alternatives for the MPE is to use them in elastomeric materials, given the needs of the rubber industry to reduce the weight of the products, and the MPE have precisely as its greatest advantage its very low density. In particular, they can be quite attractive for the footwear industry due to the marked tendency of this industrial sector to reduce weight in the soles. However, it is necessary to carry out studies on its influence on vulcanization kinetics, its compatibility with both polar and non-polar polymer matrices, the effect on mechanical, thermal and acoustic insulation properties, to mention the most relevant factors when compounds are developed in rubber.

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