Biodegradable thermosets polymers as an alternative solution to pollution generated by plastics

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Abstract. In this research work, a description was made of thermoset polymer materials and their relationship with the environment. The traditional thermoset manufacturing processes make their recycling and reuse complicated. Consequently, most products made with this type of material end up accumulating in landfills and their disposal generates a high environmental impact. This is why a description of thermoset and biodegradable polymers is made to identify the differences between them and the advantages of biodegradable materials. This being so, it is found that the scientific community presents as a proposal or alternative solution to this environmental problem the development of new methodologies and technologies to synthesize families of thermoset biodegradable materials, as for example the case of "glycix", "titan" and "hydro", and that from capital investment in science and technology processes in the area of materials engineering, by the productive sector and Universities of countries such as for example; Mexico and Argentina, managed to develop on an industrial scale biodegradable resins that can be processed by all conventional plastic molding methods and significantly reduce the carbon footprint.

1. Introduction
Thermosets are polymeric materials, fundamental in the manufacture of many of the products that we have around us [1], a very common example is the phenol formaldehyde used for the production of the body and electrical part of the computers thanks to its versatility, it is also used to elaborate the nail polishes that along with the phthalates and toluene form the group of the toxic trio, which according to the World Health Organization (WHO) [2] is related to the appearance of cancer, details that most women and men who use them do not know, because they are simply guided by a system of consumerist thinking and not by knowing what they are really using. In order to contribute to people's health and well-being, it is necessary to replace these synthetic products with products made with natural or toxic-free bases, as they are currently being developed, under a chemical-free slogan and trend, an example of which is nail polish, creating the 3-4-5 free, assuring the consumer that what they are using will not generate future damage [3]. The demand of consumers with a mostly environmentalist tendency, generates pressure on the productive sector, and through the investment of capital and the efforts between academia and science, allows to open the window to the investigation and development of new materials that manage to satisfy these needs.
2. Methodology
For the development of the present investigation of literature review, it was decided to elaborate a descriptive investigation, which has the purpose of making known different derivatives of thermostable biodegradable materials, a generality is given about thermosets, their evolution, their general characteristics, later a conceptualization of the found materials that present this characteristic is made, for later through investigations found in the literature, to evidence their applicability and impacts in the science of materials and the environment.

The sources used to extract the information were the subscription databases of the Universidad Francisco de Paula Santander, San José de Cúcuta, Colombia, and also the open access databases, generating as a result 60 articles used in the development of the review which are limited to a time window from 2005 to 2019. The search was made possible by executing the following search formulas: "green thermosets" + "biodegradable", "thermosets" + "polymers", "polymers" + "biodegradable", "thermosets" + "new materials" and "polymers". This search was made in an exploratory manner in order to identify the supporting references.

3. Biodegradable polymers
Since the beginning of the 20th century, different findings have been made about biodegradable plastics, materials that, when exposed to biological agents such as plants or the environment, decompose into the chemical elements that make them up. In 1923, due to concern for the environment, polyhydroxyalkanoate (PHA) was discovered [4,5], which is produced in nature by the action of bacteria, in 1983, the first commercial biopolyester "biopol" was produced, using the bacteria Ralstonia eutropha, glucose and propionic acid, with great benefits to nature and the plastic industry, because it reduces the dependence on oil for the manufacture of these materials, as well as the solid waste that is discarded daily on land and in the oceans, generating all kinds of waste, both solid and leached, and air pollution, through the burning of these [6].

As a result of these discoveries, today the world is developing biologically based plastics, known as bioplastics [7,8], which are derived from vegetable products, which also greatly reduces the use of oil in their manufacture. To this end, natural fibers are used, from products such as: corn, sugar cane, and soybean oil, among others. At the same time, analyses and innovations are being presented, implementing agroindustrial waste, such as the case of avocado seed, patented by "biofase" [9], which is a Mexican company that developed biodegradable plastic resin from this agroindustrial waste, [10,11] with which applications can be made in the field of Polyethylene (PE), Polypropylene (PP) and Polystyrene (PS). Although this is a great development for the care of the environment, [12] it is still not entirely feasible because the cost of producing a bioplastic is four times higher than that of producing a petroleum-based plastic.

Many renewable resources are currently being studied [13] for the design of green materials, creating composite materials which are formed by the matrix and a reinforcement which offers the possibility of improving characteristics in the polymer, such is the case of the study of the properties that would entail the addition of the coconut endocarp in the material [14]. Compared to other materials, plant fibers are generally suitable for reinforcing plastics due to their high relative strength and stiffness, low cost, low density, low CO₂ emissions, and biodegradability [15].

In the case of thermosets [16,17], several studies have been developed about the incorporation of renewable resources for both domestic and industrial use, an example to illustrate this is the incorporation of renewable and recycled raw materials in unsaturated polyester resins such as polyethylene terephthalate (PET) [18]. Work has also been carried out based on bioplastics, providing the possibility of creating a green alternative, that is, one that is ecological and sustainable, as an option to oil-based plastics [19,20], generating an impact on the plastics industry and its derivatives, so much so that the intention is also to develop paints or coatings with natural fibers that can present at least the minimum conditions in terms of their mechanical, chemical and electrical properties, among others [21].
4. Thermosets
Thermosets are infusible and insoluble polymers due to the formation of a thermally stable lattice of covalent reticular bonds [22], which makes their curing process irreversible, turning them into materials that could not be recycled until 2015 [23]. All the materials and products that surround us have a history that takes us back to the primitives, who adapted the materials they had within their reach or available in order to survive and face nature, as is the case with the wheels or the evolution of the tools we use today [24]. This was also the origin of thermosetting plastics; in the beginning, natural rubber was synthesized from the tree called *hevea brasiliensis* to make elastic products or waterproof fabrics, all of this by hand and without knowing that they would be the pioneers in the development of materials that abound in the world today [25].

From the development of rubber, new discoveries were presented to modern science as it was in the year 1828 [26], by the hand of Friedrich Wöhler, who managed to develop the synthesis in laboratory of a product made by living organisms, urea, which triggered various applications as fertilizers, drug production and in the plastics industry urea-formaldehyde resin [27,28] used to make chipboard, cosmetics and paints [29]. A decade later, after the accident of spilling rubber and sulphur on a stove, Charles Goodyear became the author of vulcanization, which turned natural rubber into a thermoset [30,31]. These historical findings have been the basis for the evolution of materials that are currently very useful, vulcanization helped rubbers to improve their properties such as resistance to abrasion, and resistance to chemical attack, without losing their natural elasticity [32].

4.1. Biodegradable thermosets
Until 2014 the words biodegradable and bioplastic were only used for thermoplastics, a classification of polymers like thermosets and elastomers, but unlike these, thermoplastics can be recycled [33,34]. Recently, researchers at the University of Amsterdam developed a thermoset biodegradable bioplastic, which breaks the pattern that only thermoplastics had these characteristics, making this material called: "glycix", the first green thermoset [35]. Initially the researchers wanted to develop a biofuel, in which glycerol and citric acid were found as components, which turned out to be the basis of this new thermoset, two substances with abundant supply and which are produced from biomass [36].

Glycix has properties such as inherent flame retardancy, good adhesion properties and low cost [37,38] It can be used for packaging, toys, rigid items used in homes and buildings, tables, lamps, as a potential substitute for packaging with PS, and also a promising application is to replace polyurethane in foam mattresses; among others. Due to this great versatility, glycix has already been tested in the industrial environment, creating immense expectations about this new polymer, which would make its mass production earlier than expected. Furthermore, researchers claim that its synthesis processing is low technology and can be easily molded by injection [39], this thermostable biodegradable polymer, has the property of easily adhering to other materials, which makes it possible for it to be used outdoors as well, combining with stainless steel, glass, etc., its decomposition occurs on contact with water, increasing its speed of decomposition depending on the degree to which the polymer has hardened and its degradation time varies from several weeks to a year [40].

Many discoveries of biodegradable materials will happen by mere chance, such as the first green thermoset, which takes us into a new era of polymers, and leads us towards a more sustainable future in which we leave aside the use of non-renewable resources for non-basic consumption. There is a growing trend towards caring for the environment through awareness and commitment to the reuse of plastics. Most of the plastic products currently produced are petroleum-based, and consumers are aware of this, so they have begun to purchase products with the bioplastic and biodegradable seal [41].

Polymers covalently bonded to chemical reagents are used as catalysts, which is the case of thermosets or ion exchange resins or applications in medicine or agriculture in which the material interacts with the environment progressively releasing the drug or fertilizer. The complexity and novelty of these materials and the fact that they are applications involving a small volume mean that there are plastic flows that are not recycled. According to reports, the sectors with the highest estimates of material consumption are the construction, automotive and packaging manufacturing.
sectors in Spain and the European Union [42]. Plastic consumption in Spain alone was 3.5 million tons in 2002, or approximately 84 kilograms per inhabitant [43]. As with other goods, the production of plastics, before their processing and use in consumer applications, involves emissions that have a significant environmental impact. In terms of air emissions, PET and high-density polyethylene (HDPE) are the most polluting, followed by PP and polyvinyl chloride (PVC) due to their manufacture.

Thermoset plastics can only be heated and shaped once, because after these molecular changes, they are cured and retain their shape and strength even under intense heat and pressure [44]. Because of their strength, thermoset plastics are a vital part of our modern world and are used in everything from mobile phones and circuit boards to the aerospace industry, but these characteristics that make them essential in modern manufacturing also make them impossible to recycle, with the result that most thermoset polymers end up in the landfill [44].

As a result, most thermoset polymers end up in landfills. Consequently, critical advances have been made in biogradability, with the design of recyclable thermosets called poly-hexahydrotriazines (PHT), which can be dissolved in a strong acid that separates the polymer chains into monomer that can be reused in new products. This dramatically shifts the concept of thermoset materials moving up the biodegradable ladder, as they could have the same applications as their non-recyclable predecessors [45].

No recycling is 100 percent effective; the innovation of these new materials accelerates the movement of the circular economy with great reduction of plastic waste in landfills. Thermoset polymers that can be easily recycled are categorized as a breakthrough in science, because polymer chains are not chemically linked to each other, thermosets are highly cross-linked, so the chains cannot be unraveled when the material is heated. This reticulation gives them strength, better physical stability and qualities that are valued in various industries but at the same time makes them difficult to recycle, because they simply end up in the garbage at the end of their useful life [46].

This suggests that it is becoming increasingly clear that the use of long-lived plastics for short-life applications is not entirely justified, especially where there is an increasing danger of environmental disturbance. The disposal of plastic waste is of great interest in surgery, hygiene, packaging, agriculture, fisheries, environmental protection, technical applications and other potential uses [47]. Most of today's plastics and synthetic polymers are obtained from petrochemicals. Conventional plastics are persistent in the environment and inadequate waste disposal treatment of plastic materials are a significant source of environmental pollution. The use of biomass is an alternative to this problem; agro-industrial waste emerges as a flagship option. However, for the sugar and food industries, it is the most promising supply option; not only is its low cost, but its conversion solves other problems at the same time, transforming waste into useful products [48]. Biodegradable plastics offer a number of advantages when compared to conventional plastics. The latter are completely degraded into compounds that do not harm the environment: water, carbon dioxide and humus. In addition, these plastics are produced from renewable sources of energy, which contributes to the maintenance of fossil (non-renewable) reserves on the planet.

The demands of the market are not long in coming, since a clear example to demonstrate this is the innovation in the automotive industry that requires plastic materials in very high quantities, the integration of plastic materials in the production of cars is today synonymous with innovation and guarantee of efficiency for the end user, the objective of mentioning these changes, is that by publicizing the innovations in raw materials that are revolutionizing the industry, automobile manufacturing generates advantages such as weight reduction and design flexibility. However, the automobile industry has promoted the development and advancement of science in new environmentally friendly materials, among one example is PP to absorb shocks generated by impacts, the industry is at the forefront and there is no doubt that it will come to use bio-based materials [49].

According to international standards, such as ASTM D6400-10 [50], ASTM D6868-03 [51], ASTM D1238-13 [52], ASTM D638-14 [53], the following must be complied with: (a) At least 90% of the organic part of the material must be converted into CO₂, in less than 6 months of contact with a
biologically active medium and (b) The resulting material must pass agronomic (behavior on plants) and ecotoxicity tests.

4.1.1. Glycix. This material has properties such as inherent flame retardancy, good adhesion properties and low cost; it can be used for packaging, toys, rigid items used in homes and buildings, tables, lamps, as a potential substitute for packaging with PS, and also a promising application is to replace polyurethane in foam mattresses; among others. Due to this great versatility, glycix has already been tested in the industrial environment, creating immense expectations for this new polymer, which would make its mass production earlier than expected. Furthermore, the creators of this material claim that its processing is low-tech and can be easily moulded by injection, it has the property of easily adhering to other materials, which makes it also suitable for use outdoors, combining with stainless steel, glass, among others [54].

4.1.2. Titan and hydro. The first material mentioned has self-repairing properties, which allow it to deform easily. Titan has a strength similar to that of animal bones and about one third of the tensile capacity of steel, when mixed with carbon nanotubes, this value can even be tripled, resulting in one of the strongest and lightest materials known to man [55]. The second material, the gel known as hydro, is a compound 70% liquid and is extremely flexible, its most important property is its ability to regenerate, when a part of this polymer is divided and placed next to each other with the "single body", they are joined or bonded together again in the same material. Hydro can be used as a powerful contact adhesive as well as being 100% water soluble [56]. This is the first group of polymers discovered in the 21st century. Most of the polymers we use today were discovered between 1930 and 1950; this is one of many examples of recyclable thermosets [57,58].

4.1.3. Biofase. It is an example of a Latin American venture. It is a Mexican company that has developed a family of biodegradable resins that can be processed by all conventional plastic molding methods. They replace PE, PP, PS applications. Ideal for plastic processing companies that wish to develop new business units oriented towards sustainability. They take advantage of the avocado seed, which is the waste of the avocado industry, reintegrating them into the productive chain, transforming the avocado seed into bioplastic resins, using the conventional methods of transformation of the raw materials. Among its bio-based products we find the avoplast resin (avoplast; commercial name of the product in Spanish), it is a hybrid that replaces up to 70% of the oil content by vegetable matter. It is biodegradable, significantly reduces carbon footprint, replaces PS, PP and PE applications, and is excellent for injection molded products such as cutlery, rigid packaging, cups, among others.

4.1.4. Arbio. It is the direct competition of biofase, a pioneer company in the incorporation of technological innovation in the field of biotechnology in Argentina. Arbio was born from a strategic alliance between the Patagonian group, which provides solutions to the production of plastics in that country, and Guangdong Shangjiu, a Chinese company specialized in the research, development, manufacture and sale of bio-based resins. In arbio, they state that their main competitive advantage is their biological-based resins, since their materials are made from plant products residing from agro-industry, which generates a low environmental impact, that is, it generates a reduced emission of carbon dioxide and the waste is biodegraded by the action of microorganisms, which represents a competitive advantage over conventional plastics. Among the arbio products we find the resin based on starch of reference and commercial denomination BOR-M-502F, according to the characteristics of the product; the granules are light yellow and of cylindrical or round form, with a smooth fragrance, absorb the humidity easily and decompose quickly by bacteria or algae, these granules are antistatic. The processing temperature of these granules is lower than that of conventional plastic, they can be easily colored. This resin can be processed on common low-density polyethylene (LDPE) extruders, sheet extruders, bag machines, 3D printers and heat-sealing machines.
5. Conclusions
According to the review we observe a worldwide trend by researchers who use various methodologies to obtain properties that allow the biodegradation of thermostable plastic materials. Among these techniques, there are biological applications such as ligninolytic fungi, or the use of agro-industrial waste for the creation of new products that do not represent a problem for the environment, it is important to highlight the products created by arbio, biofase, glycyx and others that have been designed with the principle of protection and conservation of the environment, therefore it is important to highlight this advance, since it is necessary to continue with the search for new materials.

The synthesis of glycix, titan and hydro, marks the beginning of the era of green thermosets. Through the review of the literature, the desire of researchers for the development of new materials that contribute to the health of the human being and the protection of their environment is perceived; it is expected that this culture will expand throughout the world. The development of biodegradable thermoset polymers represents an advance in what is traditionally known as thermoset polymers, which can be neither recycled nor reprocessed and their decomposition process is almost non-existent due to their properties. These are materials that are very resistant to contact with the environment; the study of environmentally friendly thermosets provides the opportunity to continue working on the development of materials with low environmental impact.

References
[1] Kalpakjian S, Schmid S 2008 Manufactura, Ingeniería y Tecnología (Ciudad de México: Prentice Hall)
[2] Brown R 1999 Handbook of Polymer Testing: Physical Methods (Marcel Dekker, Inc: New York)
[3] Carreher C E, Seymour R B 1995 Introducción a la Química de los Polímeros (New York: Reverté)
[4] González García Y et al. 2013 Revista Internacional de Contaminación Ambiental 29(1) 77
[5] Ashori A 2011 Handbook of Biodegradable Polymers: Isolation, Synthesis, Characterization and Applications (Weinheim, Germany: John Wiley & Sons)
[6] Fung L et al. 2004 Macromolecular Bioscience 4(3) 186
[7] Guerin P, Renard E, Langlois V 2010 Plastics from Bacteria: Natural Functions and Applications (Berlin: Springer-Verlag)
[8] Iwakiri M A 2014 Handbook of Polymers from Agro-industrial Waste (Toronto: ChemTec Publishing)
[9] Manyak B F 1975 Ciencia de los Polímeros (New York: Reverté)
[10] Stewart R 2008 Plastics Engineering 64(1) 16
[11] Yu L, Dean K, Li L 2006 Progress in Polymer Science 31(6) 576
[12] Arias L S, Trujillo A F 2013 Entre Ciencia e Ingeniería 7(14) 93
[13] Ruíz G, Motoya C, Paniagua M 2009 Revista Escuela de Ingeniería de Antioquia 12 67
[14] Kumar R et al. 2002 Industrial Crops and Products 16(3) 155
[15] Billing J 1975 Ciencia de los Polímeros (New York: Reverté)
[16] Illera J D, Hernández H, Niño E 2014 Revista Colombiana de Materiales 5 50
[17] Raqueza J M et al. 2010 Progress in Polymer Science 35 487
[18] Tokiwa Y, Jaruwattanawichit P 2004 Biotechnology Letters 26(10) 771
[32] Bellas García R M 2012 Formulación y Caracterización de Materiales Compuestos Integrados por una Matriz de Caño Estireno-butadieno (SBR) Reforzada con Nanoarcilla (España: Universidad de Coruña)

[33] Vitoria T B 2009 Estudio y Modelización de la Procesabilidad Mediante Moldeo por Inyección de Materiales Termoplásticos Reciclados (España: Universitat Politècnica de València)

[34] Garraín D, Vidal R, Franco V, Martínez P 2008 Residuos 104 58

[35] Halpern J M et al. 2014 Journal of Biomedical Materials Research Part A 102(5) 1467

[36] Bruggeman J P et al. 2008 Biomaterials 29(36) 4726

[37] Sakai R et al. 2013 Macromolecular Materials and Engineering 298(1) 45

[38] Amsden B, Wang S, Wyss U 2004 Biomacromolecules 5(4) 1399

[39] Lee X, Wahit M U, Adrus N 2016 Journal of Applied Polymer Science 133(40) 133

[40] Alberts A H, Rothenberg G 2017 Faraday Discussions 202111

[41] Van den Oever M et al. 2017 Bio-based and Biodegradable Plastics: Facts and Figures: Focus on Food Packaging in the Netherlands (Wageningen Food & Biobased Research: Netherlands)

[42] Castells X E, Jurado L 2012 Los Plásticos Residuales y sus Posibilidades de Valoración: Reciclaje de Residuos Industriales (Madrid: Díaz de Santos)

[43] Arandes J, Bilbao J, López D 2004 Revista Iberoamericana de Polímeros 5(1) 28

[44] Gomis A M, Beltrán Rico M 2012 Tecnología de Polímeros. Procesado y Propiedades (España: Universidad de Alicante)

[45] Oliva Civera G 2012 Plásticos Biodegradables (España: Universidad de Zaragoza)

[46] Ibeh C C 2011 Thermoplastic Materials. Properties, Manufacturing Methods, and Applications (New York: Taylor & Francis Group)

[47] Téllez Maldonado A 2012 La Complejidad de la Problemática Ambiental de los Residuos Plásticos: Una Aproximación al Análisis Narrativo de Política Pública en Bogotá (Colombia: Universidad Nacional de Colombia)

[48] Quiñones I J 2009 Informador Técnico (73) 53

[49] Ayala S L G, Sanabria F L Y 2018 Ingenierías USBMed 9(1) 69

[50] American Society for Testing and Materials (ASTM) 2010 Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions ASTM D6400-10 (USA: American Society for Testing and Materials)

[51] American Society for Testing and Materials (ASTM) 2003 Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates ASTM D6868-03 (USA: American Society for Testing and Materials)

[52] American Society for Testing and Materials (ASTM) 2013 Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer ASTM D1238–13 (USA: American Society for Testing and Materials)

[53] American Society for Testing and Materials (ASTM) 2014 Standard Test Method for Tensile Properties of Plastics ASTM D638–14 (USA: American Society for Testing and Materials)

[54] Dores C S 2018 Use of Innovative Active Packaging in Storage and Postharvest Quality of Fresh Strawberries and Dehydrated Kiwifruit Snacks (Portugal: Universidad del Algarve)

[55] García J M, Robertson M L 2017 Science 358(6365) 870

[56] Hong M, Chen E Y X 2017 Green Chemistry 19(16) 3692

[57] Garrison T F, Murawski A, Quirino R L 2016 Polymers 8(7) 262

[58] Schneiderman D K et al. 2016 ACS Macro Letters 5(4) 515