Plastic Mulch Materials

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Contributor: Cristina Abbate , Aurelio Scavo , Gaetano Roberto Pesce , Stefania Fontanazza , Alessia Restuccia , Giovanni Mauromicale

Mulches can be defined as materials that are applied or grow on the soil surface (the latter are the living mulches), in contrast to soil-incorporated materials. The use of plastic mulch films is widespread in agriculture for specialty cropping systems because of several benefits.

biodegradable mulches biodegradation soil health sustainability bioplastic mulches mulching history of mulching plasticulture

1. General Background of Mulching

1.1. History and Economic Importance

The English word "mulch" could be a loanword of the early modern age (XVI century) German word "mölsch" (soft or rotten). The two words could be also related, that is to say they could have the origin in common [1]. Finally, "mulch" could derive from Middle Dutch "malsc" [1]. The Proto-Indo-European root of the word could be "mel-" meaning "soft", with derivatives referring to soft or softened materials [2]. "Mel-" may be the source of the Greek "malakos" (soft) and the Latin "mollis" (soft) [2]. Although the etymology of the word "mulch" recalls the idea of softness, the mulching technique was also implemented with lithic materials such as stones, pebbles, and volcanic sand [3]. Lithic mulching is an ancient technique typical of agriculture in arid and semi-arid areas, and human communities distant in time and space have resorted to it from prehistoric times to the present day, and on all continents [3]. Reading the texts of the modern age, it is possible to find information about the use of plant materials to cover the soil. Giovan Vettorio Soderini, an Italian agronomist of the sixteenth century, in his "Trattato della coltivazione delle viti, e del frutto che se ne può cavare" (published in Florence in 1600), recommended placing the mulch inside the pit to plant vines. François Gentil in his "Le jardinier solitaire" (published in Paris in 1704), indicated a practice that might appear singular; he advised placing straw mulch at the foot of the trees, so that their fruits would not be damaged by falling to the ground. In the November 1778 issue of *Farmer's Magazine* (a periodical published in London), regarding the seed propagation of rhubarb, it is written: *If the seeds vegetate late in the season, they ought to be covered with mulch or moss, to preserve them in winter.* Since the early twentieth century, the attention of farmers towards mulching, made with both vegetable residues and paper, has increased [4]. In this regard, the use of tar paper as mulch began long before polyethylene (PE) was available. In fact, the first tar paper mulch, designed to defend the roots of trees from pests, dates back to 1870 [5]. In the first half of the twentieth century, some crops, such as the pineapple in Hawaii [6], have been enhanced through the innovation of paper mulching. Interest in mulching has further grown with the development of plastic materials [4]. In 1948 in the United States, PE was evaluated for the first time in agriculture with the aim of making greenhouse covers cheaper than those made with glass. However, the use of PE films as mulch began in the early 1960s when mulch applicators were developed, together with transplanters that plant directly on the mulch [7]. The use of plastic in agriculture increased considerably over the years, so much so that the word “plasticulture” was coined as a blend of the words “plastic” and “agriculture”. In this regard, at the end of the 1980s more than 3.5 million hectares were covered with plastic mulch (**Figure 1**) and nearly 450,000 tons of plastic mulch were used every year [7]. In the same period, about 80% of the mulched areas were in China (**Figure 1**). This figure appears even more surprising if considering that in 1979 only 44 hectares of mulched area were in China [7]. In the 1999–2002 period, China still had about 80% of the world’s mulched areas, despite the latter having grown to nearly 12.5 million hectares [8][9]. In 2017, the areas covered by plastic mulch reached 22 million hectares [10], 84% of which were in China [11] (**Figure 1**).

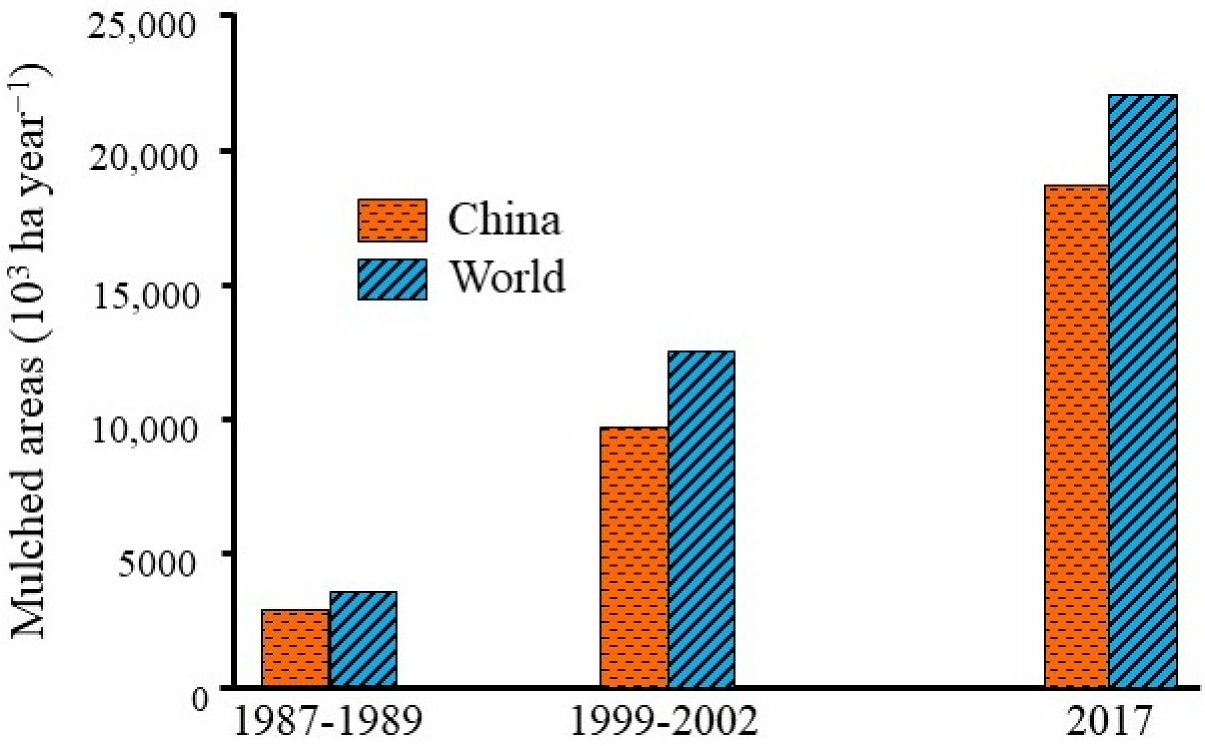

Figure 1. Mulched areas in China and in the world over the 1987–2017 period. Sources: Jensen and Malter [7]; Jouet [8][9]; Castellón [10]; An et al. [11].

Furthermore, in 2017 about 2.75 million tons of mulch film were used in the agricultural sector [12], meaning that over just thirty years the world annual consumption of plastic films increased sixfold. Plasticulture is still very widespread in Europe. In the two-year period 2018–2019, plastic mulches accounted for 25.3% of the plastic sold for crop production and for 11.2% of the total plasticulture in Europe (**Figure 2**) [13]. The European countries (EU + 3) where the most plastic films were sold in 2018 were Spain (93,000 tons) and Italy (89,500 tons), followed by Germany and France (70,000 and 57,500 tons, respectively) (**Figure 3**) [13].

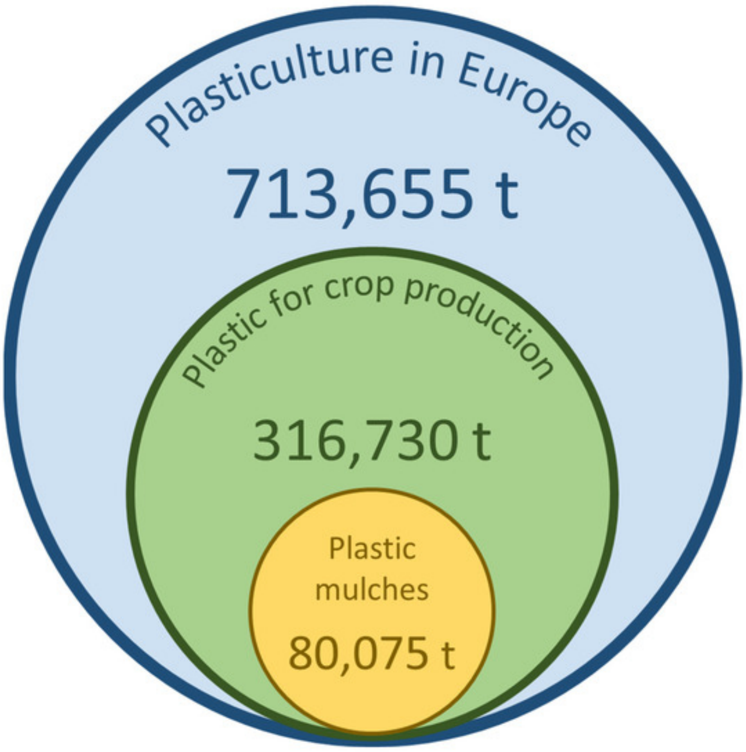

Figure 2. Venn diagram about plasticulture in Europe over the 2-year period 2018–2019. Data are expressed as tons of plastic sold. Source: APE Europe [13].

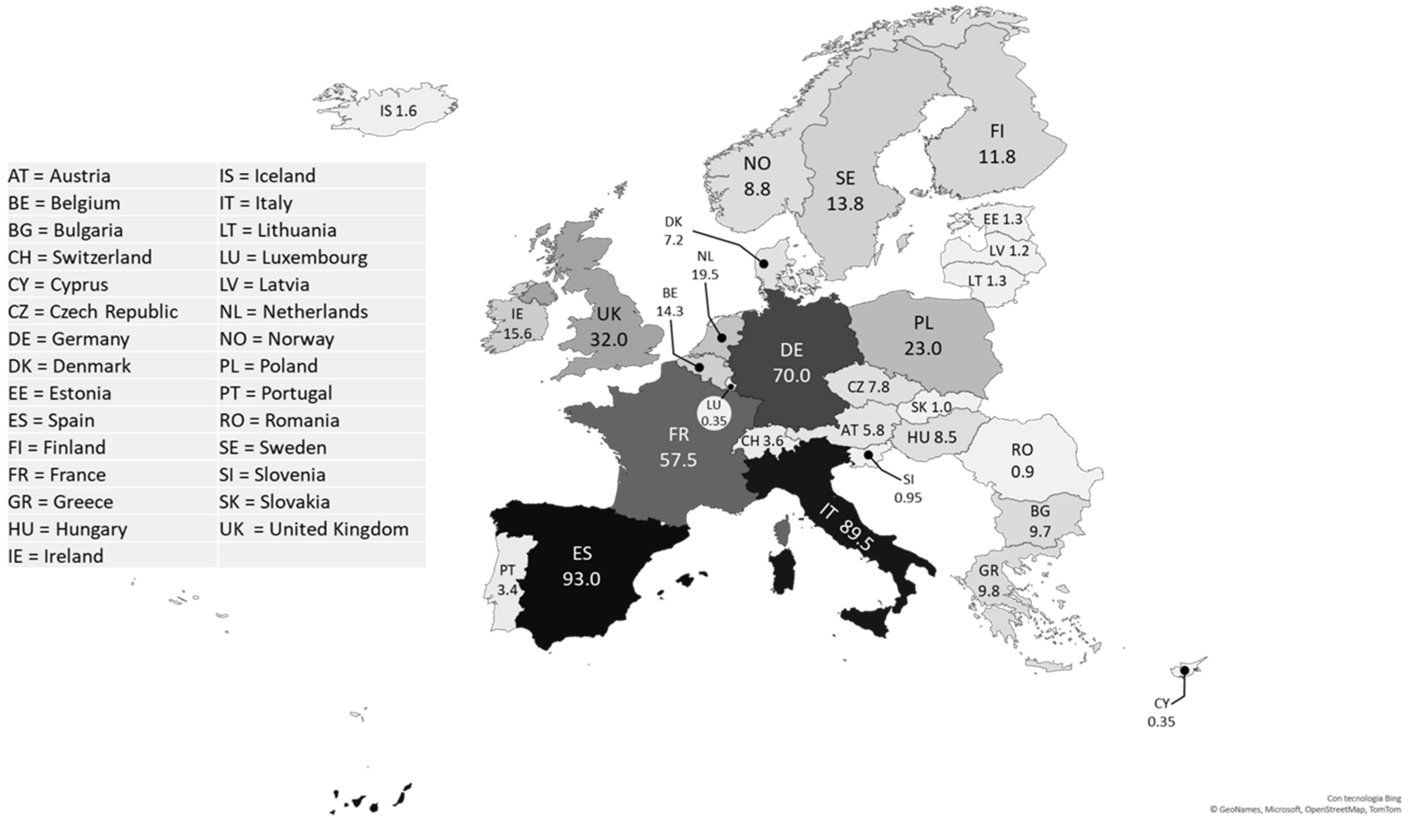

Figure 3. European film sales by country in 2018 expressed as thousands of tons. The darkness of each country in the map is proportional to the mass of plastic films sold. The two-letter abbreviations of country names are in

accordance with the ISO 3166-1 alpha-2 standard. Source: APE Europe [13].

1.2. Classification of Mulching and Main Issues

Mulches can be defined as materials that are applied or grow on the soil surface (the latter are the living mulches), in contrast to soil-incorporated materials [14]. They may provide many services to the soil: improvement of moisture content, reduction in soil compaction and erosion, mitigation of temperature excesses and defects, and improvement to plant establishment and growth [15][16]. Not to mention, organic and living mulches can improve soil nutrition, degrade pesticides, and reduce weed pressure [14][17][18][19][20]. Mulching materials can be classified into three types: organic materials (products of vegetable or animal origin), synthetic materials, and special materials (e.g., gravel); they can be used in combination, based on the specific aims [21]. **Figure 4** shows the variety of mulches in relation to the material they are made of. There are a great number of organic mulches, and these include agricultural and industrial wastes, as well as living mulches. Synthetic mulches include several types of plastic films (**Figure 4**), even biodegradable and photodegradable ones [22], as well as spray-degradable polymer films (**Figure 4**), which are very versatile and easy to apply in the field.

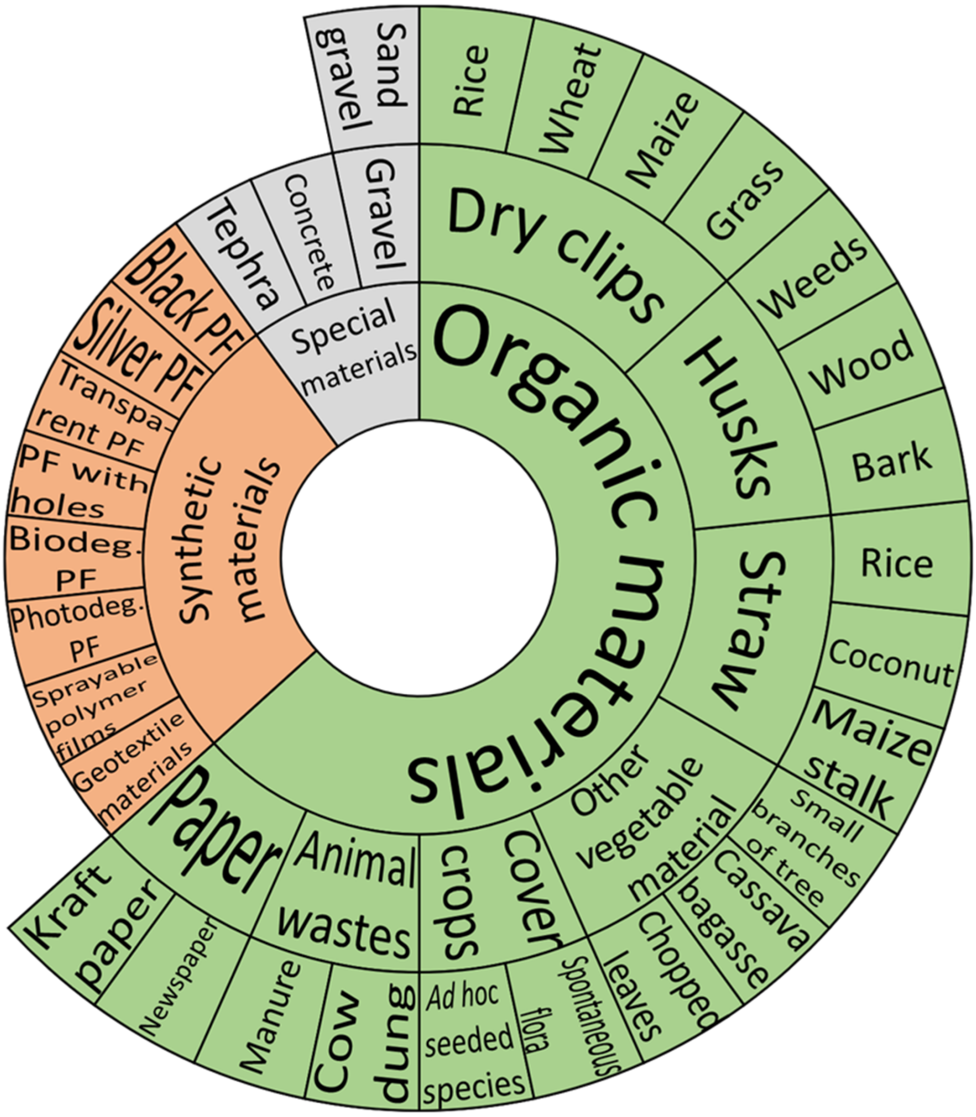

Figure 4. Mulches divided into classes of materials. Modified and adapted from Kader et al. [21]. PF: plastic film.

The choice of mulching material depends on several intersecting factors such as cost, availability, ease of application, local climate, and agronomic needs of the main crop [23][24]. The color of the plastic films, for example, affects solar radiation transmittance and thus soil temperature [25], but also influences other aspects, such as the attraction of specific insects and the control of pathogens [15]. The climatic conditions of the cultivation area must also be considered when choosing the mulching method [21]. The large-scale production of plastic films and the high persistence of the latter in the environment have raised alarms about a potential massive accumulation of pollutants in the environment [16]. Furthermore, the residues of plastic films left in the soil over time fragment and become smaller and smaller, to the point of becoming microscopic, i.e., “microplastics” [26]. Therefore, plastic films must be removed to prevent them from becoming a threat to terrestrial and aquatic fauna when they enter the food chain [16]. Plastic mulches can be recycled, however; during mechanical recycling, the films go through several stages: washing, shredding, drying, and pelletizing [27]. Obviously, all these operations have a cost. According to Le Moine and Ferry [28], the environmental issues associated with plastic mulching are aggravated by the fact that, over the years, the thickness of the films has decreased from 40 to 20 μm, then to 10 μm and even below. When they were thicker, these films were easier to recycle. Now that they are thinner, they become dirtier and therefore more difficult to recycle.

2. Plastic Mulch Materials

2.1. Polymers and Plastics

A polymer, the term for which derives from the Greek words πολυ- (poly) and μέρος (meros), literally meaning “having many parts”, is a substance composed of macromolecules. Polymers are present in nature, since they make up tissues of living organisms or perform important biochemical functions (e.g., cellulose and proteins), and some of these have important technological applications [29]. There are also polymers of partial natural origin that are synthesized from living tissues and chemically modified into “half-synthetic polymers”. Totally synthetic polymers, synthesized from low-molecular components, i.e., organic monomers [30], are mostly produced from fossil fuels such as oil and gas. Plastics are polymers that can be grouped into bioplastics and conventional plastics. The word “bioplastic”, however, can cause confusion, due to the meaning that everyone can attribute to the prefix “bio”. In fact, according to European Bioplastics [31], a plastic material is defined as a bioplastic (BP) if it is either bio-based (i.e., wholly or partially derived from biomass), biodegradable, or features both properties (**Figure 5**). Thus, contrary to common sense, some petroleum-based plastics can also be classified as bioplastics, provided they are biodegradable (**Figure 5**).

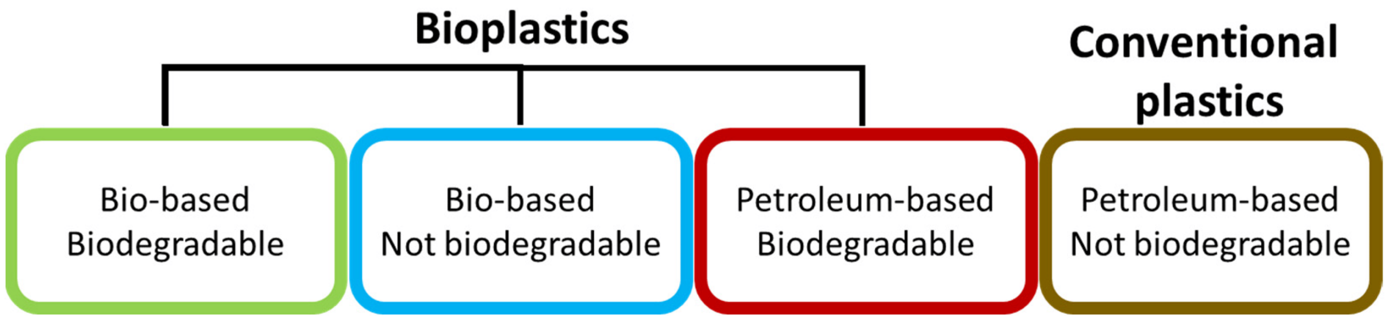

Figure 5. Classification of plastics according to origin and biodegradability.

2.1.1. Conventional Petroleum-Based Plastics (CPs)

Conventional petroleum-based plastics (also called fossil-based plastics) are artificial organic polymers, obtained from natural gas or oil, and utilized in contemporary society in every aspect of daily life [32]. One of the products of crude oil distillation is naphtha, which in turn can be transformed into various hydrocarbons by thermal cracking and fractionation. The thermal cracking of saturated hydrocarbons produces unsaturated hydrocarbons, which are molecules suitable for use as monomers in polymerization reactions [30]. Around 4% of global oil and gas extracted is employed as raw material for plastics production, and a similar amount is used as energy in the process [33][34]. Among the environmental impacts caused by plastics production, greenhouse gas (GHG) emissions are of central importance. It suffices to know that plastics caused 4.5% of global greenhouse gas emissions in 2015; moreover, 6% of global coal electricity is used for plastics production [35]. The most-used CPs in agriculture are: polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), polyvinyl chloride (PVC), polycarbonate (PC), and polymethylmethacrylate (PMMA) (**Table 1**). Some of these materials are suitable as greenhouse covers (PC and PMMA) (**Table 1**). PVC is used to produce irrigation pipes due to its mechanical and chemical resistance. One of the most-used polymers for the covering of small tunnels is EVA, due to its transparency and thermal insulation effect [36]. PP is used to produce pipes, nets, sheets, twines [37] (**Table 1**) and, as a valid alternative to PE, mulches. Compared to those made of PE, PP mulches have a lower impact resistance, but a higher service temperature and a greater tensile strength. PP is also more durable than PE; therefore, it is more suitable in perennial systems where mulch remains or is reused for several years [38]. However, the most common CP mulches are those made of PE and, more precisely, those made of low-density PE (LDPE). LDPE and high-density PE (HDPE) have the same composition, both being made up of C_2H_4, but they differ in structure. In fact, HDPE has a linear structure and no or a low degree of branching, while LDPE has a higher degree of short and long side-chain branching [39].

Table 1. Characteristics and purposes of the most-used petroleum-based plastics in agriculture. Adapted and modified from Scarascia-Mugnozza et al. [37]. LDPE: low density polyethylene; HDPE: high density polyethylene; PP: polypropylene; EVA: ethylene vinyl acetate; PVC: polyvinyl chloride; PC: polycarbonate; PMMA: polymethylmethacrylate.

Property/Purpose	Material						
	LDPE	HDPE	PP	EVA	PVC	PC	PMMA
Chemical formula	$(C_2H_4)_n$		$(C_3H_6)_n$	$(C_2H_4)_n(C_4H_6O_2)_m$	$(CH_2CHCl)_n$	$(C_{16}H_{14}O_3)_n$	$(C_5H_8O_2)_n$
Monomer molar mass (g mol^{-1})	28.05		42.08	114.14	62.50	254.28	100.12
Density ρ (kg m^{-3}) (ISO 1183)	910 ≤ ρ ≤ 925	940 ≤ ρ ≤ 965	850 ≤ ρ ≤ 900	926 ≤ ρ ≤ 950	1370 ≤ ρ ≤ 1430	1200 ≤ ρ ≤ 1220	1170 ≤ ρ ≤ 1200
Fertilizer bags	✓	✓					
Greenhouse coverings	✓			✓	✓	✓	✓
Irrigation and drainage	✓	✓	✓		✓		
Low tunnel films	✓			✓	✓		
Mulching films	✓		✓				
Nets for collecting		✓	✓				
Nonwoven/floating covers	✓		✓				
Other (rigid sheets, pots, twine, etc.)	✓	✓	✓		✓		✓
Silage films and protective covering	✓						
Vineyard and orchard coverings	✓			✓			
Woven nets (hail, wind, bird, shade)		✓					

Plastics usually contain more than one added component. If the added material is another polymer, then it is a polymer blend. There are many additives and fillers that can be compounded into the polymers for various purposes [30]. Non-ionic surfactants (esters of fatty acids and glycerine or sorbitan) are used as anti-fogging additives in the antifog films in order to allow condensation to spread into a continuous and uniform transparent water layer on the surface of films. This results in improved light transmission and transparency. Photoselective antipest films opaque to ultraviolet light are obtained with UV-absorbing additives. To improve the IR opacity of LDPE films, fillers or additives are used, especially of mineral type, such as silicates, carbonates, sulfates, and hydroxides, etc. [36]. Pigments can be used as additives in the production of plastic mulches to make them colored or black [37]. Additives can aggravate environmental problems related to plastics. In this regard, the case of phthalates (PAEs) in China is noteworthy. PAEs are broadly added to plastics in order to enhance their plasticity and versatility. Given that they are not chemically bound to the polymeric chains, PAEs can easily migrate from products and be released as xenobiotic and hazardous compounds into the environment [40]. It is an established fact that the application of plastic mulches is one of the major sources of PAEs in China's soils [40].

2.1.2. Bioplastics (BPs)

The world production of bio-based polymers amounted to 3.5 Mt in 2018 [41], 3.8 Mt in 2019, and 4.2 Mt in 2020 [42]. A constant growth is therefore observed; however, these values represent roughly 1% of the annual world production of fossil-based polymers. Based on the observed growth trend, the quantity of bio-based polymers produced in 2025 is expected to be 6.7 Mt [42]. In 2020, a small fraction (0.038%) of the biomass produced in the world was demanded for bio-based polymers production. This fraction amounts to about 4.8 Mt and is divided as follows: 37% are made of glycerol, 24% of starch, 16% of sugars, 12% of non-edible plant oil, 9% of cellulose, and 2% of edible plant oil (**Figure 6**) [42]. The percentage of agricultural land used in the production of biomass destined for bio-based polymers is 0.006% [42], a percentage that is six times lower than the above-mentioned 0.038% relative to the share of biomass. This disproportion has two explanations. On the one hand, more than a third of the feedstocks (37%) is represented by glycerol (**Figure 6**), which is a by-product of biodiesel production and is therefore obtained without land use [42]. On the other hand, starch and sugars, which represent, respectively, 24% and 16% of the total feedstocks (**Figure 6**), come from high yielding crops [42]. However, from the 4.8 Mt of feedstocks, only 1.9 Mt of bio-based components are obtained, while the rest (2.9 Mt) are made up of losses of feedstock and intermediate products, together with waste products (**Figure 6**) [42]. From 1.9 Mt of biobased components 4.0 Mt of bio-based structural polymers (completely or partially bio-based) were obtained in 2020 (**Figure 6**) [42].

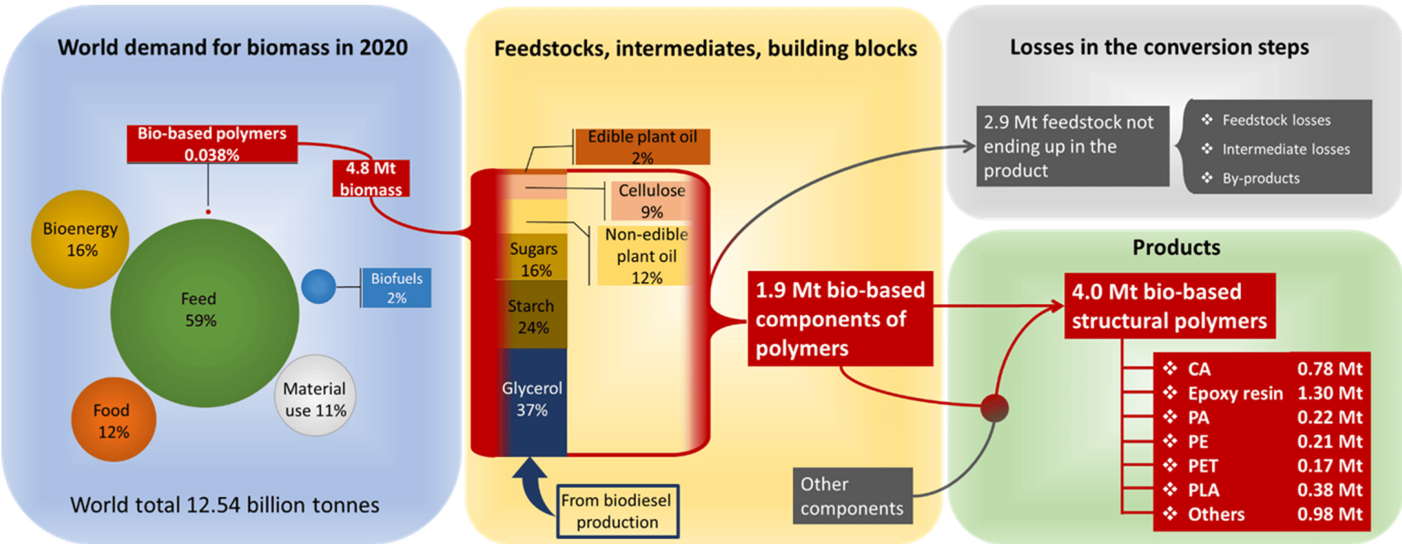

Figure 6. Diagram of the relationships between the biomass to produce bio-based polymers and bio-based structural polymers produced worldwide in 2020. Modified and adapted from Carus [42]. CA: cellulose acetate; PA: polyamide; PE: polyethylene; PET: polyethylene terephthalate; PLA: polylactic acid.

As seen above, an important part of bio-based plastics derives from agricultural raw materials, which compete with food production for arable land, water, and other resources [43]. Furthermore, bio-based plastics can have a certain environmental impact. In fact, their production cause acidification and eutrophication, as their raw materials are obtained using inputs such as pesticides, herbicides, and fertilizers [44].

Below is an overview of the most common BPs employable as feedstocks to produce mulches.

Starch is a plant reserve carbohydrate, synthesized from glucose, which in turn is produced through photosynthesis from carbon dioxide and water. For this reason, it is a biodegradable, renewable, and inexpensive raw material. However, starch has poor physical properties, since it is a hydrophilic substance that dissolves in water and becomes brittle when it is dried. It is therefore necessary to mix or change the composition of the starch before it can be used as a biodegradable mulching material [45]. There are mulching films based on starch mixed with biodegradable polyesters to improve their mechanical characteristics, while maintaining their biodegradability.

Along with starch, aliphatic polyesters are the most widely used bio-based feedstocks to produce biodegradable plastic mulches. The aliphatic polyesters are polymers suitable for use as biodegradable plastics, thanks to the ease with which they are degraded by lipolytic enzymes and microorganisms [46].

Polyhydroxyalkanoates (PHAs) are a family of biological polyesters consisting of 3-hydroxyalkanoic acids (HA) as monomer units. PHAs have been studied as possible substitutes for CPs, since they can be synthesized and degraded by living organisms [47]. The properties of PHAs depend on the composition of their monomers. There are, in fact, short-chain HA (3–5 carbon atoms), medium-chain HA (6–14 carbon atoms), and long-chain HA (more than 14 carbon atoms) [48]. Moreover, PHAs can be homopolymers (i.e., consisting of the repetition of the same monomer) or heteropolymers (i.e., consisting of different monomers). Finally, with respect to their origin, it is possible to distinguish natural PHAs, semi-synthetic PHAs and synthetic PHAs [49]. PHAs are synthesized by Gram-positive and, especially, Gram-negative bacteria [48]. However, the production of PHA by microorganisms in bioreactors poses technical problems that limit its economic convenience. On the other hand, the biosynthesis carried out by transgenic plants, which only need water, mineral salts, CO_2, and light, makes the production of PHAs more economical and respectful of the environment. Furthermore, plants, unlike bacteria, do not degrade PHAs [50]. Despite that more than 150 types of PHA have been obtained [51], there are few mulching films based solely on PHAs on the market, probably due to the high costs of production and poor mechanical properties [52]. Fortunately, one of the valuable characteristics of PHAs is their compatibility with other polymers (especially polylactic acid), with which they can form the so-called polymer alloys [53].

Polylactic acid (PLA) is another bio-based and biodegradable polymer used in agriculture. The molecular brick of which PLA is made is lactic acid (LA), a hydroxy acid that exists in both the dextrorotatory and levorotatory forms. The main feeds of LA-producing bacteria are glucose and maltose from wheat, potatoes, sugar-beets, corn, and sugarcane molasses [54]. The production of PLA passes through some stages that can be summarized as follows: obtaining LA by lactic fermentation or by chemical synthesis, LA transformation into lactide monomers, and polymerization of lactide monomers [55]. PLA possesses good mechanical strength and, compared to other biopolymers, it is less expensive and available in larger quantities. However, it has characteristics that make it unsuitable for mulch on its own [56]. In fact, the glass transition temperature (~60 °C) of PLA makes it not easily accessible to microorganisms under normal conditions of use [56]. Additionally, PLA is quite hard, resulting in embrittlement and poor thermostability [56]. Fortunately, PLA is compatible with other polymers, such as PHAs. The blend of PLA and PHAs creates a synergistic effect, due to the complementarity of their respective characteristics [53]. Biodegradability of PHA/PLA mulches prepared using both spunbound and meltblown processing have been evaluated [57][58]. The results indicate that spunbond mulches biodegrade more slowly than meltblown ones, suggesting that the former are more suitable for making longer-lasting products, such as row covers and landscape fabrics [57][58].

There is also **bio-based PE**, obtained through the polymerization of ethylene produced with the catalytic dehydration of bioethanol [59], but unfortunately it is not biodegradable [43].

The most common fossil-based polymers used to make biodegradable plastic mulch are **poly(butylene-adipate-co-terephthalate) (PBAT)**, **poly(ε-caprolactone) (PCL)**, and **poly (butylene succinate) (PBS)** [60]. PCL and PBS are aliphatic polyesters (such as PHAs and PLA [61]); the former has a relatively low melting point (60 °C) and is often mixed with starch to increase biodegradability, while the latter has physicochemical properties like polypropylene’s [60]. PBAT has a high elasticity and mechanical strength, as well as resistance to water and oil [60]. Its biodegradability in soil has been demonstrated using ^{13}C-labeled PBAT, which made it possible to distinguish the CO_2 produced by the mineralization of the soil organic matter from that resulting from the degradation of the polymer. It was also possible to recognize the ^{13}C in the microbial biomass of the soil [62].

Protein-based mulching films combine biodegradability with N content, which increases their agronomic value; another advantage is the fact that they can be blended with other polymers [63]. They can be of animal origin, such as the mulching sprays obtained from protein hydrolysates, derived from waste products of the leather industry [64], or can be derived from the proteins that make up the body of scavenger insect larvae, which live on decaying organic matter [65]. Both products would fall within the scope of the circular economy. The protein-based films can also be of plant origin; for example, the secondary product resulting from the extraction of oil from soy is a protein-rich flour that can be used as a raw material to produce such films [66]. Unfortunately, soy protein-based films are brittle and water sensitive and therefore require plasticizers, such as glycerol and graphene, to improve their mechanical properties [66][67]. Zein is a hydrophobic, alcohol-soluble protein isolated from corn. It is a thermoplastic material very suitable for film production and can be used to make food packaging [68]. Zein-based mulching films have been evaluated as a possible economic and environmentally friendly alternative to polyethylene mulching, with reference to soil water losses by evaporation on greenhouse-grown tomatoes [69].

Paper mulches were included here, although cellulose is not a bioplastic, to complete the framework of mulches that are bio-based and/or biodegradable. The main raw material of paper mulches is vegetable fibers, but research on traditional paper mulches currently focuses on reinforcing agents that can affect mulch performance [5]. The conventional papermaking process results in mulches with insufficient mechanical properties to meet application requirements in the field. It is true that the performance of paper mulch can be improved by chemical additives, but it is equally true that the latter increase the cost of the product up to making it applicable only to highly profitable crops. Furthermore, such substances can have a negative environmental impact [5]. The performance of traditional paper mulch can be improved through solution impregnation, with which composite coated paper is obtained. Research on paper mulches has also extended to paper production processes, such as the non-woven technology papermaking process, which uses mineral fibers, plant fibers, and chemical fibers as raw materials [5]. Paper mulches are much more biodegradable than plastic ones, but this virtue must be accompanied by lower costs and improved performances if the paper is to spread as mulch in different environmental conditions.

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