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Chemical Modification of Starch with Synthetic

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Abstract

An alternative for solving the environmental pollution problems generated by conventional plastics, it is the chemical modifications graft-type of the starch with synthetic polymers of post-consumer and in situ polymerizations on the starch granules. The starch modified by this methodology allows to counteract the disadvantages of both polymers such as the little or no biodegradability of the synthetic polymer and the poor mechanical properties of the starch. In the present study, a review on the chemical modification of starch with synthetic polymers by grafting is carried out. Factors affecting the copolymerization reactions of starch-g-synthetic polymer were analyzed, for example, their chemical nature, solubility, size and length of polymer chains, temperature, catalyst and starch/amylose content, as well as their characterization chemistry and the potentials applications of this copolymer.

Keywords: starch, synthetic polymer, graft copolymer, biodegradable

1. Introduction

Due to environmental pollution generated by conventional plastics such as polyethylene (PE), polypropylene (PP), vulcanized rubber, polystyrene (PS) and polyvinyl acetate (PVC), to name a few, several investigations have been carried out to generate materials that can compete or be an alternative to the excessive use of these plastics because these are not biodegradable. From this point of view, the use of natural polymers such as starch can contribute to reduce the negative impact of conventional plastics. However, materials made from starch alone generate plastics, which have important disadvantages such as their high affinity for moisture and poor mechanical properties. An alternative for solving these disadvantages is the chemical modifications of the starch with synthetic polymers of postconsumer and in situ polymerizations on the starch granules. These chemical modifications are called graft-type copolymerizations because the synthetic polymer chains are chemically bonded to the surface of the starch granule, as if these were hair extensions (**Figure 1**).

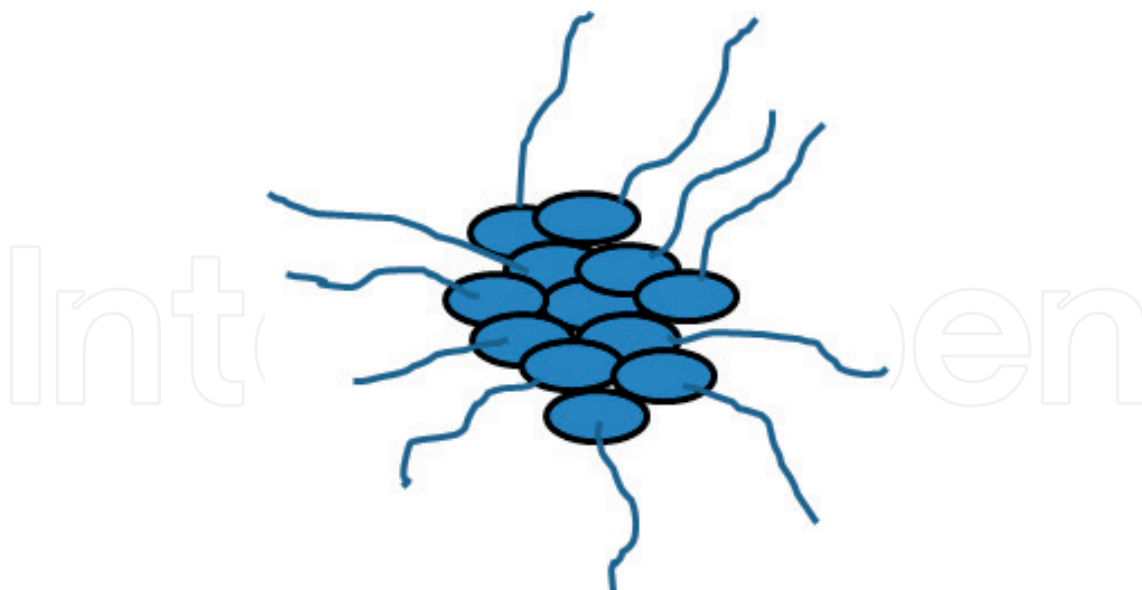


Figure 1. Graft copolymerization of starch-g-synthetic polymer.

Numerous investigations have been reported on physical modifications (i.e., blends or composites) between starch and synthetic polymers [1–5] and few investigations on chemical modifications of copolymerization between these two polymers [6, 7]. This represents a good opportunity to recycle the existing plastic or generate new biodegradable materials through copolymerization reactions. The modified starch by this methodology allows to counteract the disadvantages of both polymers such as the little or no biodegradability of the synthetic polymer and the poor mechanical properties of the starch, to mention some characteristics that generate a wide range of applications of the resulting copolymer. For this reason, the chemical and physical knowledge of synthetic polymer and starch is vital to propose and carry out a possible synthesis of starch-g-synthetic polymer. This chapter analyzes the chemical modification of starch with synthetic polymers by grafting, and factors that affecting the copolymerization reactions of starch-g-synthetic polymer are analyzed, for example, their chemical nature, solubility, size, and so on.

2. Factors affecting the copolymerization reactions of starch-g-synthetic polymer

In order to carry out the chemical modification of the starch with some synthetic polymers, we have to take into account diverse chemical and physical factors. Some of these factors are described below.

2.1. The chemical nature of synthetic polymers

The chemical nature of the polymers is a very important factor to consider for the copolymerization reactions of the starch. The knowledge of the chemical compatibility between

the natural and the synthetic polymer, that is, its hydrophilic and hydrophobic nature, will allow to propose a reaction medium to carry out a chemical interaction between these two polymers. For example, polyethylene is a non-polar semi-crystalline polyalkane, which would hardly carry out a copolymerization reaction with the starch by simply mixing both polymers. But the addition of some compatibilizing liquid between PE and starch could facilitate its chemical interaction [1]. Based on the commercial classification of the synthetic polymers and their functional group, the compatibility between the starch and each of the synthetic polymers could be predicted (**Table 1**).

For example, synthetic polymers classified commercially with numbers 2, 4, and 5 would be more difficult to combine with starch compared with classified numbers 1, 3 and 6. On the other hand, there is a great diversity of synthetic polymers classified with number 7 that present chemical compatibility with the starch. The degree of compatibility of the functional groups of the synthetic polymers with the starch has the following order:

Carboxylic acids > acid anhydrides > esters > acid halides > amides > nitriles > aldehydes > ketones > alcohols > mercaptans > amines > ethers > sulfides > alkenes > alkynes > halogenides > nitros > alkanes.

The chemical interaction of the starch with the functional groups of the synthetic polymers results in the production of graft-type copolymers. This type of chemical modification of starch is of great interest worldwide and represents an opportunity to recycle synthetic polymers or to generate materials that are more environmentally friendly and at the same time represent a chemical and physical challenge to improve the properties of starch. Starch graft copolymers are becoming important materials worldwide due to their potential applications in agriculture, medical, and food sectors [8], to mention a few examples.

2.2. Solubility

The solubility of the starch and the synthetic polymer in a given solvent plays a very important role in defining the process or the medium of copolymerization, that is, in homogeneous phase

Synthetic polymer	Commercial classification	Functional group
Poly(ethylene terephthalate), PET	1	Ester
High-density polyethylene, HDPE	2	Alkane, ethyl
Polyvinyl chloride, PVC	3	Vinyl
Low-density polyethylene, LDPE	4	Alkane, ethyl
Polypropylene, PP	5	Alkane, propyl
Polystyrene, PS	6	Aromatic, arylethyl
Others	7*	—

*This number is assigned to more than 100 synthetic polymers.

Table 1. Classification and functional group of synthetic polymers.

or heterogeneous phase [9]. The solubility of a polymer is a function of its chemical nature, chemical structure, molar mass and temperature, to mention some factors that intervene in this. For example, two chains of the same polymer but of different molar mass, the smaller molar mass chain in a given solvent is dissolved more easily than the larger polymer chain. On the other hand, branched polymers are more difficult than their polymer chains to be solvated compared to that of a linear polymer. Natural polymers usually have more complex structures than synthetic polymers; therefore, natural polymers are more difficult to dissolve than synthetic polymers. Polymers having a degree of cross-linking between their chains are more difficult to have their chains solvated than the same polymer but with less or no cross-linking. The structure of the coupling or folding between the different chains of a polymer is important to predict their degree of solubility from the cavities that are generated from these arrangements. On the other hand, the dissolution process of a polymer is different than that of chemical compound or small molar mass. In the case of polymers is a slow process and is composed of two stages or phases. The first stage is called the solvent diffusion process, where the solvent molecules diffuse into the polymer chains producing a swollen gel. The second step is called the decoupling of the polymer chains, that is, the dissolution of the polymer. The latter will occur if the interaction forces between the polymer chains are minor compared to the interaction force of the polymer chains with the solvent. Otherwise, the polymer will only swell, but will not dissolve, as occurs in crystalline and cross-linked polymers [10]. The lighter fractions of a polymer dissolve first, leaving the fractions of high molar mass insoluble. The properties of the polymers in solution are determined by the structural characteristics of the solvated macromolecular chain. The mechanism of dissolution of a polymer has been investigated by several researchers, including Ueberreiter [11] and Krasicky et al. [12]. In the liquid or solution state, the physical and chemical interaction of the two polymers, starch and synthetic polymer, is facilitated by increasing the degrees of freedom of the atoms and the interaction of their functional groups. From the solubility parameters, this interaction or the compatibility between the two polymers and the solvents can be predicted, this parameter reflects the degree of its cohesive energy. In the literature, there are different proposals for determining these parameters, for example, using the Flory-Huggins solution theory, the Hildebrand solubility parameters, van Krevelen and the Hansen parameters [13–15]. The latter being the most used because it takes into account the forces of dispersion (δ_d), the hydrogen bonds (δ_H) and the polar forces (δ_p) of polymers and solvents, Eq. (1).

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \quad (1)$$

where δ^2 is the solubility parameter.

In **Table 2**, solubility parameters of some synthetic polymers and some solvents determined from the Hansen equation are presented.

If the difference between the solubility parameters of the solvent and the polymer is small, the compatibility of the polymers with the solvent is favored because thermodynamically its entropy of mixing would increase as well as the decrease the value of the Gibbs free energy of the solution. A rule widely used to determine the polymer-solvent miscibility is.

$$\delta_2 - 1.1 < \delta_1 < \delta_2 + 1.1 \quad (2)$$

where δ_1 is the solubility parameter of the polymer and δ_2 is the solubility parameter of the solvent [18].

The solubility parameter of a polymer can be determined from experimental results considering the solubility parameter, the average of the range of solubility parameters of the solvents in which it is completely soluble [19].

The properties of the polymers in solution are determined by the structural characteristics of the solvated macromolecular chain. The three hydroxyl groups of the starch are very skilled at their hydration; however, the starch granule is not solvated by water molecules at room temperature (**Figure 2**).

Starch is a polymer, which is difficult to dissolve due to the complexity of its chemical structure and its spatial arrangement. However, it is slightly soluble in some solvents due to the physical interaction of the three hydroxyl groups found along its main chain or its side chains with the

Polymer	δ (cal/cm ³) ^{1/2}	Solvent	δ (cal/cm ³) ^{1/2}
Polytetrafluoroethylene	6.20	Diethyl ether	7.10
Polyisobutylene	7.70	Hexane	7.24
Natural rubber	8.15	Decane	7.74
Polybutadiene	8.38	n-Butanol	7.81
polyethylene	8.67	Cyclohexane	8.20
Poly(n-butylmethacrylate)	8.75	Toluene	8.88
Poly(ethylmethacrylate)	8.95	Benzene	9.02
Polystyrene	9.12	Chloroform	9.26
Poly(methylmethacrylate)	9.25	Acetone	9.74
Polycaprolactone	9.35	Octanol	10.23
Neoprene GN	9.38	Acetic acid	10.44
Poly(vinylacetate)	9.40	Pyridine	10.60
Poly(vinyl chloride)	9.55	n-Propanol	11.72
Poly(ethyleneterephthalate)	10.10	Dimethyl formamide	12.15
Polyacrylonitrile	12.75	Acetonitrile	12.54
Starch	13.25	Ethanol 99.9%	12.83
		Dimethyl sulfoxide	13.03
		Methanol	14.64
		Ethylene glycol	16.91
		Glycerol	17.63
		Water	23.40

Table 2. Values of the solubility parameters of Hansen [13, 14, 16, 17].

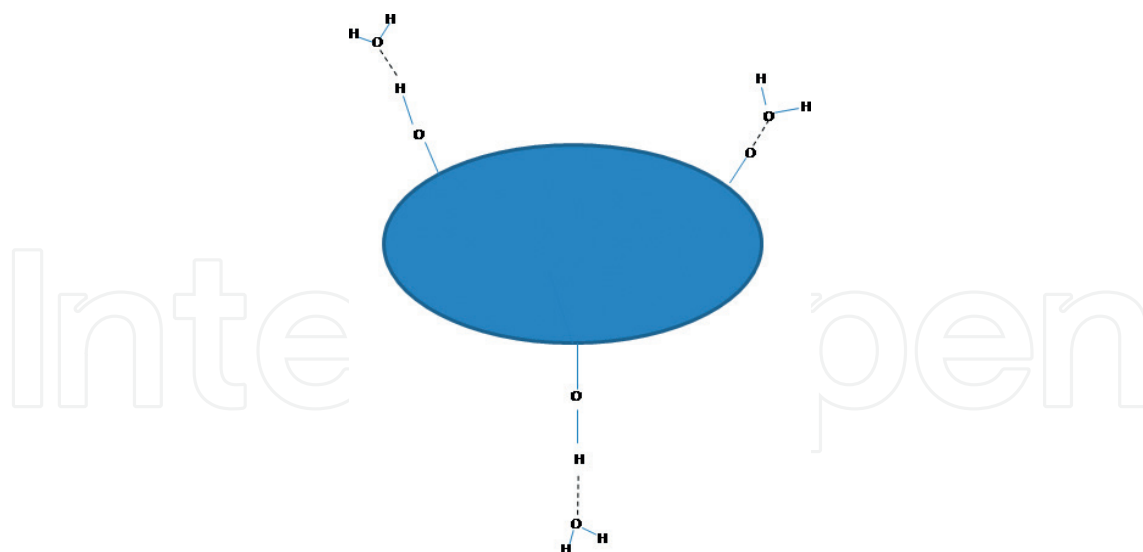


Figure 2. The starch granule remains hydrated but not solvated by water molecules at room temperature.

solvent. For example, starch is slightly soluble at room temperature in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), partially soluble in water at temperatures above 80°C, partially in water/ethanol mixtures in the temperature range of 30–50°C and sparingly soluble in chloroform, to mention some examples. With respect to the two polymers that form the starch, the amylopectin is soluble in hot water and the amylose is not soluble (gelatinization process). Taking into account the partial solubility of starch, the search for solvents or mixtures of solvents is very important for carrying out the chemical modification of this natural polymer with synthetic polymers because in a dissolution reaction medium, it is more favored in comparison with other polymerization medium, for example, in mass and emulsion. In a dissolution reaction, there would be more chemical interaction between the two polymers, there would be no secondary reactions (the solvent would be inert), furthermore, in this reaction medium, it is easy to separate the solvent at the end of the synthesis, the released heat is absorbed by the solvent and the rate of reaction decreases, and generally, the presence of the solvent decreases the temperature of the synthesis. The investigations reported in the literature on the chemical modifications of starch with synthetic polymers are in the heterogeneous phase [20].

The solubility of the polymers is also very important to define their area of application, for example, at the biological level, they can be applied in tissue regeneration, in drug release and in membranes; at the industrial level in the manufacture of microchips and plastic materials, to mention some examples. Also, the solubility of the polymers is very important to propose its possible route of recycling.

2.3. The size of the polymer chains

Many polymers will contain molecules having many different chain lengths. It is known that the size of the chains of a polymer is one of the main factors that determines or governs its physicochemical properties, its processing behavior and consequently its possible applications.

For example, properties such as impact strength, viscosity and elasticity are in function of short chain length, medium chain length and long or large chain length, respectively [21]. The

polydispersity index (PI) of a polymer is an important parameter to know the homogeneity or heterogeneity of the length of the chains of a polymer. The PI is determined by Eq. (3).

$$PI = M_n/M_w = M_z/M_w \quad (3)$$

where M_n , M_w and M_z are the number average molar mass, mass average molecular mass and mass average molecular mass-mass, respectively. A value of $PI \geq 1$ indicates polydispersity and a value of $PI = 1$ means that the length of the polymer chains or molecular weight is equal. The molar masses of M_n , M_w and M_z are governed by the mechanism of the polymerization reaction and by the conditions under which it was carried out [22]. This represents a steric hindrance between the two polymers for that the chemical bond between them can be given [23, 24].

Thus, it is easier to graft or anchor on the surface of the starch a chain of smaller size of the synthetic polymer than a chain of large size due to its steric hindrance or the resulting degrees of freedom with the use of a compatibilizer (**Figure 3**).

This compatibilizer will facilitate chemical and physical interaction with larger size chains of the synthetic polymer. For example, Mani et al. [25] synthesized the starch-g-PCL compatibilizer to improve the compatibility with blends of starch or PCL; they found that their mechanical properties are higher than that of a starch/PCL blend. On the other hand, Wootthikanokkhan et al. [26] obtained the starch-g-PLA compatibilizer, which improved its compatibility with starch or PLA and the physical properties of starch.

2.4. Catalyst

The selectivity or development of a catalyst for synthesizing graft copolymers may vary greatly depending on the synthetic polymer to be used. This selectivity also depends on the temperature, pressure, concentration, particle size and chemical nature of the catalyst, whereby a copolymerization reaction is catalyzed under certain specific conditions.

A particular catalyst does not act in the same way in all the reactions on which it can act. It is of vital importance to understand the catalytic phenomenon to maintain the stability and

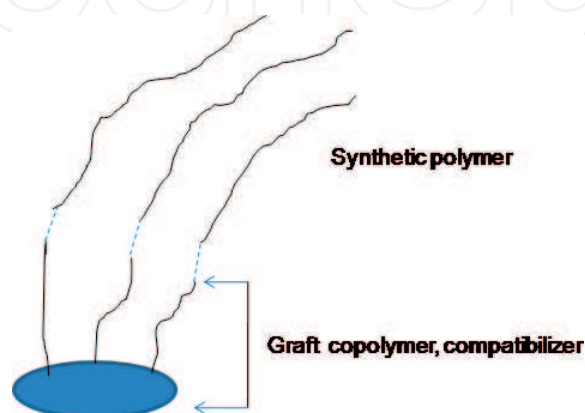


Figure 3. Compatibilizer with synthetic starch-g-polymer.

activity of the catalyst during the copolymerization as well as its process of its separation from the reactor once the copolymer is obtained. The chemical nature of the catalyst plays an important role in proposing a mechanism of copolymerization, separation or purification of the product obtained.

A variety of catalysts have been used in the synthesis of the starch-g-polymer synthetic graft copolymer. Some catalysts used in the synthesis of starch graft copolymer with synthetic polymers are presented in **Table 3**.

The graft copolymerization reactions of the starch are mainly in heterogeneous media (different phases), i.e. by heterogeneous catalysis. The choice of a catalyst for the synthesis of the graft copolymer is mainly based on the function of the synthetic polymer used. Generally, the catalyst

Graft copolymer	Catalyst	Yield (%)	Reference
Starch-g-lactic acid	Sodium hydroxide, NaOH	33.6	[27]
	Ammonia water, NH_4OH	58.9	[28]
	Sulfuric acid, H_2SO_4	75.0	[29]
Starch-g-PCL	Tin(II) 2-ethylhexanoate, $\text{Sn}(\text{Oct})_2$	40.0	[30]
	Trimethyl aluminum, $\text{Al}_2(\text{CH}_3)_6$	58.0	[31]
	Molybdenum compounds	84.0	[32]
Starch-g-PMA	Ceric ammonium nitrate, $\text{H}_8\text{N}_8\text{CeO}_{18}$	41.0	[33]
	Ammonium nitrate, NH_4NO_3	58.0	[34]
	Enzyme horseradish peroxidase, HRP	45.0	[35]
Starch-g-PS	1-ethyl-3-methylimidazolium acetate ([EMIM]Ac)	100.0	[36]
	Potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$	66.0	[37]
	Potassium persulfate/amine	32.5	[38]
Starch-g-PAN	Ceric ammonium nitrate, $\text{H}_8\text{N}_8\text{CeO}_{18}$	94.7	[39]
	Ceric ammonium nitrate, $\text{H}_8\text{N}_8\text{CeO}_{18}$ /sodium hydroxide	87.3	[40]
Starch-g-PB	Potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$	10.0	[41]
Starch-g-PGA	Sodium hydroxide, NaOH	4.2	[42]
Starch-g-PLA	Tin(II) 2-ethylhexanoate, $\text{Sn}(\text{Oct})_2$	52.0	[43]
Starch-g-PBA	Enzyme horseradish peroxidase, HRP, hydrogen peroxide (H_2O_2) and acetyl acetone (Acac)	5.6	[44]
Starch-g-poly(ethylacrylate)	Warm distilled water	27.5	[45]
Starch-g-poly-(N-methylacrylamide-co-acrylic acid)	Potassium perdisulfate, $\text{K}_2\text{S}_2\text{O}_8$	85.4	[46]

Table 3. Some catalysts used in the synthesis of graft copolymers.

used in the synthesis of the synthetic polymer is employed in the synthesis of the graft copolymer. The starch/catalyst mass ratio is a function of the degree of substitution of the hydroxyl groups of the synthetic polymer. It is known that the greater the amount of catalyst, the faster the rate of synthesis of the copolymer but with smaller synthetic polymer chain length sizes [27, 47].

2.5. Temperature

Stability of the starch against temperature is a very important factor to consider for the synthesis of the graft copolymer. It is known that the starch granule begins to fracture or degrade at 85°C in the presence of water and temperature above this range increases the degradation. The formation of starch films by the casting method occurs at about 85°C (gelatinization temperature) in approximately 20 min. On the other hand, it is possible to carry out graft-type copolymerization at temperatures higher than 100°C with the starch granules having thermal stability at these temperatures.

This is mainly because the heat generated at these temperatures is absorbed by the other components (reactants or catalyst) of the copolymerization while the activation energy is reached to convert from reactants to products, **Figure 4**.

The starch granules are prone to initiate its degradation when the copolymerization synthesis is finalized. This is because it is very important to determine the time of synthesis to avoid the degradation of the starch granule and the generation of ashes; these ashes would generate impurities and then cause darkening of the product. The temperature and the reaction time are primarily a function of the chemical nature of the synthetic polymer and the catalyst as well as of its concentration in the reaction medium. For example, in the synthesis of the starch-g-PGA graft copolymer, with temperature higher than 180°C, potassium hydroxide and microwave irradiation were used [42].

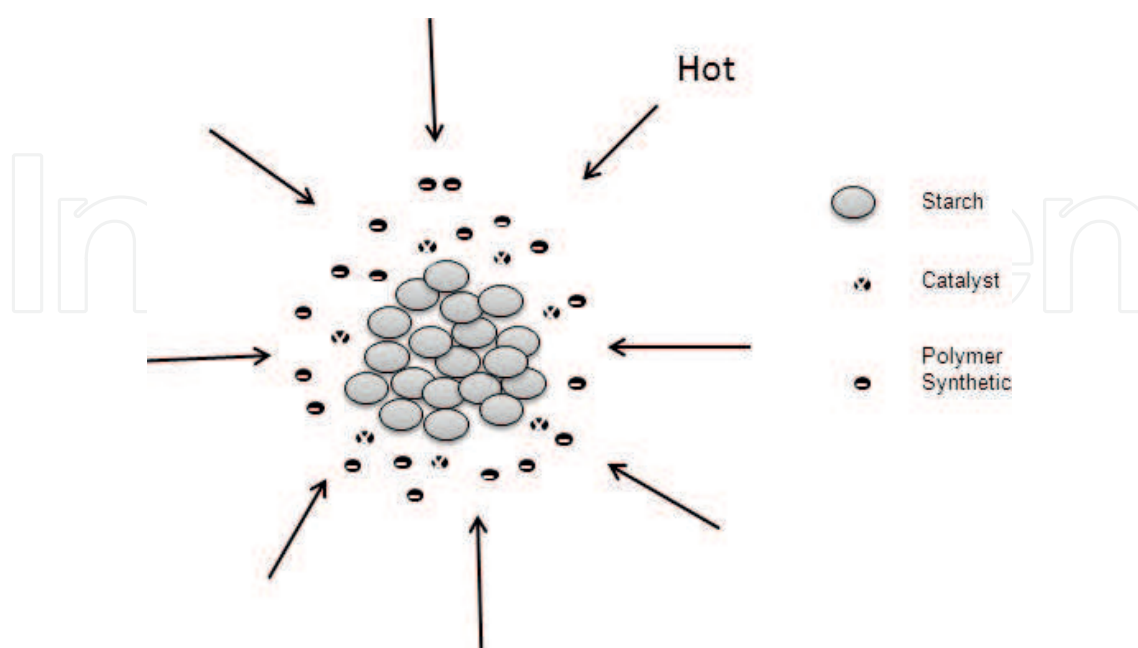


Figure 4. Thermal stability of starch.

Ramírez-Hernández et al. [32] carried out a mass polymerization for the synthesis of starch-g-PCL using a temperature range of 110–150°C. In the case of a mass copolymerization, one of the physical properties to be considered is the melting temperature of the synthetic polymer, if it presents in the reaction. This datum is important because it would allow to predict the degradation of starch granules occurs during the mass chemical reaction at the determined time. It is known that the starch begins to decompose above 85°C and if the melting temperature of the synthetic polymer is much higher, the degradation of the starch granules will be greater. Another important temperature to be known is the glass transition temperature of the synthetic polymer. If this temperature is above or below the room temperature, it would affect the physicochemical properties of the graft copolymer but this will depend on the desired mechanical properties of this copolymer.

2.6. Proportion of amylose/amylopectin and relation of the parameters of graft reactions

Starch is a polysaccharide of vegetable origin, stored in the form of granules, of complex structure found mainly in cereals (maize, rice, wheat, etc.), tubers (potatoes, sweet potatoes, yucca, etc.), legumes (pea, bean, chickpea, etc.) and fruits (mango, banana, etc.) but are also found on stems, leaves and even pollen. This semicrystalline polysaccharide consists of two polymers of α -D-glucose called amylose and amylopectin. The proportion of amylose/amylopectin and the form of the granules determines the physicochemical and functional properties of the starch granules, and consequently their use. For example, high amylose content facilitates film formation and chemical modification, but is poorly soluble in water and is more difficult to degrade with respect to a high amylopectin starch. **Table 4** shows some ratios of amylose/amylopectin reported in the literature.

According to the literature, a simple helical structure for amylose has been proposed and in the case of amylopectin, a double helix (see **Figure 5**). This arrangement of amylopectin generates an ordering of the helices, and therefore, favors its crystalline zones and decreases free space. In the case of amylose, the simple helix favors the amorphous zones with more free space between the polymer chains.

These free spaces favor the interaction with other polymer chains as the synthetic polymer. From the granule form, the amylose/amylopectin ratio and its diameter, the area of surface

Source	Moisture (%)	Starch (%)	Proteins (%)	Lipids (%)	Ashes (%)	Amylose (%)	Amylopectin (%)
Rice	16.0	83.60	0.45	0.80	0.50	25.0	75.0
Corn	13.0	85.92	0.35	0.60	0.10	27.0	63.0
Wheat	14.0	84.59	0.40	0.80	0.15	25.6	74.4
Potato	19.0	80.41	0.06	0.050	0.40	21.0	69.0
Plantain	6.6	90.00	1.60	1.70	0.10	35.0	65.0

Table 4. Amylose/amylopectin content [44–46, 48, 49].

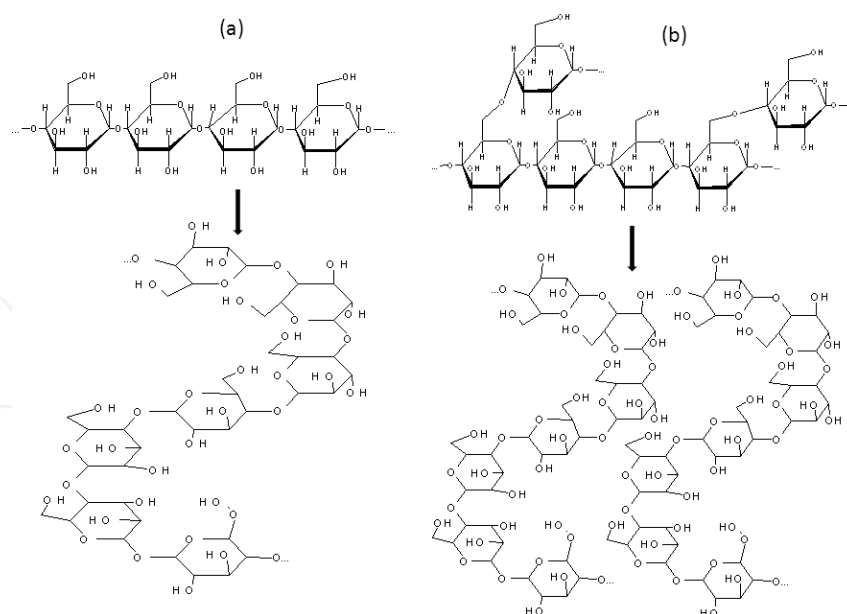


Figure 5. Structure of amylose (a) and amylopectin (b).

reactivity (R) of the starch granule can be estimated assuming that the amylose as the only component on the surface of the starch Eq. (4).

$$R = \log A \cdot Dp \cdot 3/1\mu^2 \quad (4)$$

where A is the area of the granule and Dp is the degree of polymerization. Some values of R are presented in **Table 5** for some sources of starch.

These R values are an approximation because these values consider that all the granules have the same morphology and do not take into account the possible proportion of amylopectin present on the surface of the starch granule.

The relation of the parameters of graft reactions depends on two polymers to be studied, for example, starch-g-PE and starch-g-PCL are presented in **Figure 6**.

Source	Granule form	Diameter ^a (μm)	Amylose area (μm ²)	R [*]
Potato	Oval	5–100	102–37,669	4.78–7.35
Corn	Spherical/polyhedron	2–30	50–11,309	4.47–6.83
Wheat	Spherical	2–10	50–1256	4.47–5.87
Rice	polyhedron/oval	3–12	113–1809	4.83–6.03

^{*}Using a Dp = 200.

^aAlcázar-Alay and Almeida Meireles [49].

Table 5. Values of the area of surface reactivity (R) of the starch granules.

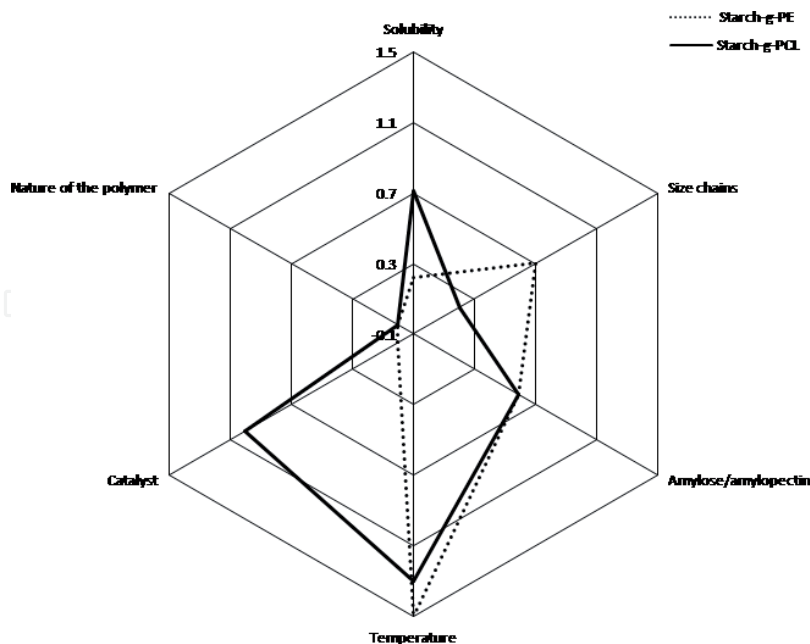


Figure 6. Relation of the parameters of graft reactions.

The solubility of the two graft copolymers depends mainly on the size of the chains of the polymer grafted on the surface of the starch granule and the chemical nature. The greater the chain length, the lesser is the solubility and vice versa, the shorter its chain length major is its solubility. This is mainly due to steric hindrance to the hydrophilic character and hydrophobic nature of the two polymer chains. The starch-g-PE graft copolymer has less solubility and its grafted chain length is greater than the starch-g-PCL. The proportion of amylose present in the starch source is important because this favors the graft reaction; in this case, both copolymers are obtained using the same source of the starch (banana starch) and the same amylose/amylopectin ratio. The presence of a catalyst in the copolymerization reaction favors the decrease of its synthesis temperature. In the case of the synthesis of the starch-g-PCL copolymer when a catalyst is used, the synthesis temperature is lower compared to the synthesis of the starch-g-PE which does not employ a catalyst and this uses a higher synthesis temperature. In both copolymers, a synthetic and a natural polymer is used; grafting a natural polymer onto the surface of the starch granule would be very difficult due to its steric hindrance since these are generally polymers of high molar mass and large chain length.

2.7. Chemical identification of the graft copolymer

In the synthesis of a graft copolymer of starch-g-synthetic polymer, the verification that the chemical reaction was carried out between the natural polymer and the synthetic polymer is of vital importance because of this experimental evidence, it is possible to explain all the physicochemical properties of the graft copolymer. There are a variety of instrumental techniques reported in the literature to characterize the chemical bond of graft type. The most common is attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). FTIR allows a quick and qualitative identification of the functional groups present in the copolymer; however, it is very difficult to identify from this technique, a chemical bond resulting from

the union between two polymers as the starch and synthetic polymer. One of the possible reasons is the amount of this chemical bond in the graft copolymer compared with the rest of the chemical bonds of the copolymer is very small. The intensity of this signal would be expected to be weak and could be overlapped with some other vibration of the copolymer. The vibration signals of the $\alpha(1-4)$ and $\alpha(1-6)$ bonds of the starch are approximately at 1024 and 994 cm^{-1} , respectively. These two vibrations correspond to carbon and oxygen (C–O) interaction [32, 50]. In the case of graft copolymerization involving the carbon (C) atoms of the synthetic polymer and the oxygen (O) atoms of the starch, the vibration signal of this chemical bond would become overlapped. However, the decrease in the intensity of some signals of the graft copolymer spectrum, such as the hydroxyl (OH) group of the starch compared to that of the homopolymers (previously to this analysis, the separation of homopolymers, which did not react and the catalyst), this would indicate that very probably the chemical bond existence between the natural and synthetic polymer, but it is a necessary assistance of other instrumental techniques such as nuclear magnetic resonance (NMR). One of the requirements for obtaining a liquid NMR spectrum is the solubility of the sample in some deuterated solvents. In the case of starch, it is a polymer with high molecular weight, which generates a low solubility in common deuterated solvents such as deuterated chloroform and deuterated water; however, it is partially soluble in DMSO. In the literature, a variety of solvents have been reported for obtaining a magnetic resonance spectrum of starch, but in many cases, the resolution of these is poor. An NMR spectrum (^1H and ^{13}C) would allow to identify with certainty whether there was a chemical bond between the synthetic polymer and the natural polymer. Two of the typical signals of a ^1H NMR spectrum of the starch are at 5.11 and 4.57 ppm, which correspond to the $\alpha(1-4)$ and $\alpha(1-6)$ bonds, respectively. These two signals in a spectrum of ^{13}C NMR exhibit a chemical shift of 100.45 and 64 ppm, respectively. In this same spectrum, a chemical shift between 100 and 175 ppm could represent the chemical bond of the graft copolymer, in the case of an interaction of carbon (C) and oxygen (O) [51, 52]. Scanning electron spectroscopy (SEM) allows the identification of changes in the morphology of the starch granule in the case of a graft copolymer or if it is only a physical mixture of the two polymers. In the SEM micrographs reported in the literature, it has been found that the graft copolymer of starch-g-synthetic polymer favors the formation of clusters or aggregates, whereas in a blend, the synthetic polymer covers the surface of the starch granules due to its physical interaction with the synthetic polymer [20]. The X-ray diffraction technique will allow to analyze the increase or decrease in the crystallinity of the starch or the synthetic polymer as a result of its chemical interaction. In the literature, it has been reported that a decrease in the crystallinity of the synthetic polymer is an indicative of the presence of the graft copolymer [53, 54]. The instrumental technique of thermogravimetric analysis and differential scanning calorimetry would corroborate a decrease in the crystallinity of the graft copolymer with respect to that of homopolymers through the decrease in the intensity of the signals and its displacement, for example, in the decomposition and melting temperatures. The BET technique allows to verify a decrease in the surface area of the starch granule due to the synthetic polymer grafts onto it [55–57]. There are other instrumental and physicochemical techniques that allow to complement the verification of the chemical bond of the starch with the synthetic polymer through the measurement of its physical and chemical properties. The chemical bond of the starch with the synthetic polymer is necessary to corroborate it through a set of instrumental techniques and not only using one of these techniques.

2.8. Applications of the starch-g-synthetic polymer graft copolymer

Worldwide research is being carried out to generate materials more environmentally friendly and that these become an alternative to compete with conventional plastics. The synthesis of graft-type copolymers between starch and synthetic polymers is a serious alternative to obtain biodegradable materials with good physicochemical properties. The applications of these copolymers are widely depending on the source of starch and the synthetic polymer (**Table 6**).

Graft copolymers	Applies	References
Starch-g-lactic acid	Material with excellent degradability	[27–29]
Starch-g-PCL	In food packaging, drug delivery, bags and flavored biodegradable materials	[30–32]
Starch-g-PMA	Food packing, biomedical fields, coating and adhesives, drag reduction, textile industry and preparing biodegradable hydrogels and agricultural mulch films	[33–35, 58]
Starch-g-PS	in the production of paper, textiles and food additives, as well as being a commonly used biotemplate and carbon precursor in materials research	[36–38]
Starch-g-PAN	In the field of biomedicine and pharmacy such as soft contact lenses, super absorbents, drug-delivery system, polymeric dispersions, pigments and improved high gloss papers coated with the coating color compositions, soil conditioners, additives for paper and textiles, adhesives, enhanced oil recovery and sanitary goods	[39, 40, 59]
Starch-g-PB	Also disclosed are paper coating color compositions comprising the polymeric dispersions and pigments and improved high gloss papers coated with the coating color compositions	[41]
Starch-g-PGA	Copolymer allows it to have many potential applications in drug delivery, food, water treatment, cosmetics and other fields. More detailed rheological property studies of starch-PGA graft copolymers are needed to explore their potential applications	[42]
Starch-g-PLA	An expected improvement in their processability and biocompatibility due to PLA branches can be utilized in a wide range of engineering, bioengineering and medical application areas, which will be the subject of our future investigations	[43]
Starch-g-PBA	This material provides an attractive alternative for the preparation of modified starch for industrial applications how a thermal stabilizer	[44, 60]
Starch-g-poly(ethylacrylate)	The sorbent could be used successfully used for five consecutive adsorption–desorption cycles, which indicated its high reusability	[45]
Starch-g-poly-(N-methylacrylamide-co-acrylic acid)	The graft copolymer can be used as a biodegradable Hg (II) ions adsorbing agent for the removal of toxic Hg (II) ions from the waste water enriched with Hg (II) ions.	[46]
Starch-g-PVA/HA	Biomedical applications	[61]
Starch-g-AAm	Waste water treatment (flocculants), polyvalent metal cation sorbents, biodegradable superabsorbent for hygienic, agricultural and cosmetics purposes, paper industry, textile industry, petrochemical and mineral recovery	[62]
Starch-g-poly(benzyl methacrylate)	Environmentally friendly materials which are promising materials such as fillers, stabilizers, modifiers, matrices or plastics which can replace nonbiodegradable and compostable petroleum-based plastic materials	[63]

Table 6. Applications of some starch-g-synthetic polymer graft copolymers.

3. Conclusions

Synthesis of starch-g-synthetic polymer graft copolymers is increasing worldwide because this copolymer is an alternative for the generation of biodegradable materials and good physico-chemical properties to compete with conventional plastics. In order to carry out this synthesis, it is necessary to review several factors such as the chemical and physical properties of the homopolymers to propose the most suitable conditions for the copolymerization reaction. The solubility of the two homopolymers in a solvent is very important to facilitate the graft copolymerization and its chemical characterization. However, the higher the solubility, the lower is the value of the molar mass grafted onto the starch granule, that is, the lengths of the grafted polymer chains decrease. The use of homopolymers of similar nature and the presence of a catalyst favor the copolymerization reaction and the decrease in their synthesis temperature, respectively. Synthesis of starch copolymers with polyhydrocarbons and hydrophobic polymers is limited; however, graft compatibilizers of starch-g-synthetic polymers can be synthesized to favor their copolymerization. The chemical characterization of the graft copolymer must be carried out through a set of instrumental techniques to corroborate the chemical bond of the starch with the synthetic polymer. The knowledge about this type of synthesis is very promising for the reduction of synthetic polymers discarded into the environment.

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