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AGRO-MATERIALS: A BIBLIOGRAPHIC REVIEW

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Abstract :

Facing the problems of plastic recycling and fossil resources exhaustion, the use of biomass to conceive new materials appears like a reasonable solution. Two axes of research are nowadays developed : on the one hand the synthesis of biodegradable plastics, whichever the methods may be, on the other hand the utilization of raw biopolymers, which is the object of this paper. From this perspective, the “plastic” properties of natural polymers, the caracteristics of the different classes of polymers, the use of charge in vegetable matrix and the possible means of improving the durability of these agro-materials are reviewed.

Keywords :

Agro-material, biopolymer, biodegradable, polysaccharide, protein, lignin, fiber, lipid

Table 3. Comparison of the mechanical resistance of various natural and synthetic fibers (Mohanty, 2000b).

Table 4. Use of agricultural waste or co-products in agro-materials.

INTRODUCTION

By creating materials easy to transform, hydrophobic and biologically inert, the plastic polymer industry has allowed the industrialization of many applications on a large scale. The food processing industry, one of the greatest users of polyolefin, would not have been able to develop so rapidly without plastic packagings.

However, several decades of intensive exploitation for common uses have caused an accumulation of wastes in our environment, source of visual and olfactory nuisance, and have polluted maritime environments (1). Apart from combustion for energy production which comes up against the need to reprocess fumes and the foreseeable limitations of carbon dioxide release, and recycling which comes up against the problem of selective sorting out and cleaning of the rejected materials, an alternative is to minimize the quantities of non-degradable plastic materials with biodegradable and eco-compatible substitutes.

But there are several possibilities regarding the choice of raw materials and the means of synthesis. The choice of renewable raw materials is in line with the necessity of limiting the exhaustion of the Earth’s reserves in fossil fuels (2) : at their present consumption rate, it is forecast that these reserves will run out in 80 years time (for oil), 70 years (for natural gas) and 700 years (for coal) (3). Even if for certain authors the ecological assessment is no more favourable for the hydro-biodegradable polymers which arise (4) than for oxo-biodegradable petrochemical synthetic polymers (5), the use of a fossil raw material will be acceptable only if it can be entirely recycled or for essential technical applications.

The first mean of substitution is the synthesis of biodegradable plastics, or rather hydrobiodegradable polymers. They can be classified in several categories : biosynthetic (polymer synthesis is done in the plant by genetic modification), semi-biosynthetic (a fermentation process allows the synthesis of polymers) and chemosynthetic (chemical synthesis using vegetable monomers) (6). All those which have already been commercialised are polyesters or amide polyesters. Even though their synthesis or extraction are still costly, these products are backed by large industrial groups because of a strong demand for «green» products.

Some natural polymers can also be extracted and chemically modified to produce thermoplastics (7). Cellophane is a classical example, but other cellulose, starch and vegetable oil derivatives have been designed. They are issued from renewable resources, but most of them are not biodegradable. Thus bearing their production cost and weaker properties, the competition with petrochemical polymers is oft unbalanced.

With the developments of biodegradable materials, other researchers are trying to use directly the biomass constituents or reserve polymers to manufacture materials (8). The conception of these «agro-materials» is therefore based on the knowledge acquired in vegetable biology about the structure of biopolymers, in the food processing industry about their physico-chemical properties and not only about the science of polymers. The most classic example is that of starch. Reserve polysaccharide in many vegetables and in particular in cereals, has already been used in loose-fill packagings such as Flupis® or Eco-Foam® (9)

and in certain commercial biodegradable plastics such as the Mater-Bi® (10). But other natural constituents can also be used, modified and/or associated for the design of biodegradable materials.

After a concise presentation of the physicochemical properties of some biopolymers, notably their strong water affinity, which induce their flowing properties and “plastic” character, the specific characteristics and the uses of most common ones are discussed. Then the full details of the addition of natural charges in the literature compositions are presented. Finally the last part of the review concerns the considered means to ensure a better water resistance to the processed agricultural matter so that the application field of “agro-materials” may be broadened while preserving their biodegradability.

PLASTIC PROPERTIES OF BIOPOLYMERS

To consider the processing of natural polymers, these need to have “plastic” properties. The flow theory, related to the glass transition phenomenon in the amorphous areas and the fusion phenomenon in the crystalline parts of polymers, comes directly from the thermal rupture of the many weak interactions which link the polymer chains (11). Then they can acquire a mobility which allows them to move in relation to each other, which, on a macroscopic scale, results in the flow of the matter. Having been done the forming, the structure stiffens, by re-establishment of the interactions between the macromolecules during the cooling (thermoplastic) or by formation of covalent bonds (thermosetting).

The transformation of vegetable matter is linked to the same phenomena, but its study is often more complex for two main reasons : the diversity of polymers structures and involved interactions, and the possible modification of their organization at all stages of extraction and processing. What distinguishes it is that the more influent non-covalent interaction is in most cases the hydrogen bond, which is strongly water sensitive.

Plastification

The role of water

The main polymers of vegetable or animal matter contain polar functions capable of linking the water molecules by hydrogen interactions with hydroxyl groups for polysaccharides, amines for proteins, phenols for lignins... According to the type and structure of the biopolymer, there are many possibilities of interactions with water, more or less intense, which define its water holding capacity (12). It is represented and then modelled with a moisture sorption isotherm – plot of water content (expressed as mass of water per unit mass of dry material) versus the relative vapor pressure- characteristic of the biopolymer (13). Under normal humidity conditions (a_w=0.6 : 60% air humidity), this water content can vary between 4 and 20% (14) and balances with the atmospheric humidity.

To give to biopolymers thermoplastic properties, the presence of water, natural plasticizer, or of another plasticizer, is in most cases essential. Natural structures have relatively low degradation temperatures (15) and the energy necessary to break the weak interactions between the chains is close to the energy which causes the degradation of these chains. The presence of a plasticizer separates the macromolecules and facilitates their movement related to thermal excitation. Two methods are therefore used to plastify and process the vegetable matter : adding water and maintaining the mixture under pressure to avoid its evaporation (16) during the transformation or using organic plasticizers with higher boiling temperatures.

Except for those which, like lignins, are essentially linked amongst each other by «hydrophobic» interactions, the thermal and rheological properties of biopolymers are therefore highly dependent on the amount of water contained in the mixture. As it is admitted that biopolymers have essentially an amorphous structure (13), in particular after an extraction process, there are many studies and some models have been developed to study the variations in temperature of glass transition according to their hydration. Thermal, or thermo-mechanical properties of starch (17; 18), wheat gluten (19; 20), corn zein (21), soy proteins (22), sunflower proteins (23) or amorphous components of wood (24) for example have been reported.

Therefore water must be considered as a full constituent of most biopolymers. Although it makes the processing delicate, this affinity for water is an essential property of biopolymers which it is necessary to understand to develop agro-materials.

1-1-2- Organic plasticizer

The low boiling temperature of water is problematic : transformations necessarily occur at high temperature to lower sufficiently the viscosity of the mixtures. The use of another organic molecule is therefore necessary. This molecule must be polar to ensure compatibility with polymers and small in order to penetrate the macromolecular network. The molecules used are polyols (25), or other small molecules such as urea (26). But it is essentially glycerol, available and cheap, which is used, because it allows a net reduction in the glass transition of the mixtures (21; 27), and has suitable physical properties (28). Its presence causes in the materials a consequent increase in elongation accompanied by a reduction in breaking stress (table 1) (29). For the manufacture of flexible films, the use of a plasticizer is essential. Recent works show that the interactions nature between the polymer chains and the plasticizer is determinant in material properties, so new molecules are now on test (30).

Organic plasticizers have another role, rarely mentioned, in the creation of agro-materials. It allows the preparation of materials which can be preserved before the processing. The amount of water contained in the biopolymers in balance with ambient atmosphere is not sufficient to obtain a suitable flow, particularly for a forming by injection-moulding (16).

Starch

Starch is the most common reserve polysaccharide. In its native state it is partially made up of crystalline granules insoluble in water. These are constituted of linear polymers (amylose) and of ramified polymers (amylo-pectin) of α-D-glucose. The crystallites are made up of short chain amylo-pectin while the amorphous areas have a lot of ramification. Although amylose is in general the minority component of starch (between 20 and 30% in mass (31)), its linearity guarantees better flowing properties. That is why starch rich in amylose, is preferred (9; 32).

To be used as thermoplastic matrix, the granular structure of starch must be destroyed to form a homogeneous amorphous phase (10). This destruction can be obtained by chemical means, that is by swelling of the amorphous parts then destroying the crystalline parts, by temperature increase and water absorption. A chemical agent such as urea favorizes granules destruction by breakage of the hydrogen bonds in the crystallites. But the most used method is extrusion, the thermo-mechanical treatment makes it possible to obtain an amorphous phase in a slightly humid conditions (27).

Starch destructured and plastified in this way (TPS : thermoplastic starch) acquires, thanks to the length of its chains and to its repeated monomeric units, flowing properties close to those of thermoplastics from petrochemistry such as polyethylene (PE) or polypropylene (PP). It is therefore used as a matrix, or as a co-constituent in a mixture with other thermoplastics in certain commercialised biodegradable plastics : Mater-Bi® (33), Novon®, Biotec® (6). It is also present in most of the biodegradable compositions of biopolymers for the design of all types of materials : expanded materials, films, injection grades, compression grades...(tables 1 and 2)

Starch plastification is a very much studied phenomenon (34; 35). The influence of the amylose/amylo-pectin ratio (36), of the extrusion conditions (humidity, temperature, pressure, shear) (18) and of certain chemical agents on viscosity (37; 38), on starch solubility and water absorption have been reported in many works.

Proteins

Soybean proteins are the first biopolymers from agriculture which have been used for the manufacture of moulded materials. Indeed, in the 30´s, Brother had started manufacturing parts for Ford cars with a phenol-formaldehyde/soybean flour mixture (39). But he had stopped due to the costs of extraction and to the emergence of synthetic plastics.

Proteins are polymers formed essentially from 20 primary aminoacids. This results in many possibilities of bondings and structures and in complex and varied properties. The ones used for the manufacture of materials are those found in greatest quantities in the natural matter exploited : reserve proteins of grains (soybean, sunflower...), cereal co-products (gluten, zein...) or proteins of animal tissue structure (collagen, keratin...).

The polypeptide chains are linked together by a large number of different interactions (40) : steric constraints, Van der Waals interactions, hydrogen links, electrostatic interactions, hydrophobic interactions and disulphide covalent bonds. They are therefore organized according to the chain of aminoacids in stable and complex structures which are classified according to a growing scale of dimension : secondary, tertiary and quaternary. Under the effect of temperature, pressure or of a chemical agent, this organization can be partially destroyed or modified. But while with starch the destructuration brings about an amorphous fluid phase, the denaturation of proteins releases the core groups of the structure which can be more hydrophobic than the surface groups, depending on their stabilisation environment. In a polar environment the structure forms with polar residues in surface and hydrophobic ones inside, and vice versa. Under thermal effect, the chains become mobile but their movement is restricted because of the structure ramification, the increase in the hydrophobic interactions intensity due to temperature (41) and to coagulation which follows denaturation (42; 43). Proteins can thus also be « plastified » but they form a phase that is not as fluid as that of starch. As shown by the results of the processing of proteins, compression is often more suitable (44; 45). With the exception of gelatine, only starch-protein mixtures are used in injection-moulding (46; 47). But these properties are naturally dependent on the nature of the proteins (the aminoacids composition is potentially different from one protein to another) for the manufacture of materials.

1-3-1- Gelatine

Gelatine is produced by transforming collagen by structure splitting and depolymerization (48). A semi-crystalline protein is obtained, having a simplified structure, and whose main property is its relative water affinity. Thus, in the presence of water, gelatine absorbs many times its weight in water, and a temperature increase to 50ºC causes a dissolving of the inflated grains leading to the obtention of a homogeneous liquid.

Gelatine can therefore, just like starch, be moulded directly by injection with a suitable humidity/temperature combination. The manufacture of capsules (16) is actually one of the oldest industrial uses of agro-materials. It is used in biodegradable compositions as the main constituent of the matrix (49), in a mixture with starch (50) or in biofilms for medical applications (51). To answer to the solubility problem in this last field, reticulation (see 3-2-2) is used but a direct chemical treatment of collagen permits to obtain by casting insoluble films too (52).

But it is mainly its adhesive properties, as indicated by the etymology of the word collagen, that are used in the area of materials. A gelatine binder dissolved in water can, for instance, be used in compression moulding of raw vegetable residues (53).

1-3-2- Soybean proteins

Soybean production covers 60% of American needs in oil and fat, therefore soy proteins are the most widespread proteins of vegetable origin. That is why they were the first to be studied and why they are the subject of the greatest number of works.

The soybean proteins used are reserve cytoplasmic corpuscles constituted essentially by two majority globulin fractions, the 7S (β-conglycinine) and the original 11S (glycinine) (54).

Hexameric 11S native protein	⟶	2 trimerics 7S	⟶	6 monomerics 3S	⟶	polypeptide α polypeptide β

The use of soybean proteins for the manufacture of materials has been intensely developed since 1994 in the Iowa State University Research Foundation. That team developed a formulation grade for compression (44), for injection (55), for the manufacture of expanded materials (56), and for sheet extrusion (57).

In every case, the soybean proteins were worked at their isoelectric point to reduce their sensitivity to water by increasing the intensity of ionic interactions. On the other hand, the reticulate character of soybean proteins hinders the flow. Thus, certain authors also try to avoid their denaturation, which in general renders them less soluble (the aqueous extraction of proteins cause the burying of hydrophobic groups in the structure core), by working at low temperatures (58). And they are often treated with a reducing agent to break the disulphide bonds which link the α and β polypeptides (59). In this way, the mobility of the chains before the processing is improved, and after the forming these bonds can re-establish themselves to strengthen the structure by sulphydryle-disulphide exchange (60).

But most of the time, in the case of injection-molding, they are associated to starch (25; 61; 62; 63) to improve the water resistance of the starch-based materials, or to lignins (64) for their mutual affinity (table2).

Soybean proteins are also used to make films (54; 65; 66; 67). Their low oxygen permeability would make them suitable for use in packaging, limited by their low water resistance (table1).

They are from now on the reference for proteic materials, sunflower proteins which are structurally very similar have been used to make thermopressed objects (68) and films by casting (69) and Salmoral made some comparisons between soybean, chick pea or white and black bean protein-based materials (70; 71).

1-3-3- Wheat gluten and maize zein

Gluten and zein are complex proteins associated to glucides and lipids. They represent about 10% of the dry weight of flour and are obtained after extraction of the grain starch. Made up by 80% reserve proteins, two types of proteins can be distinguished in the case of wheat : glutenins, polymeric proteins which give the flour its viscous character ; and gliadines, monomeric proteins which are at the origin of the elastic properties.

These proteins have largely been studied in the food processing industry and have been used for the first time for their filmogenic properties in 1972 (72) (table1). As in the case of soybean, the use of a reducing agent helps to improve the processability by increasing the polydispersity of protein polymers (58). The density of the disulphide bonds is of one bond for every 100 monomeric units(73).

Although these complexes still contain polysaccharides, their relative hydrophobicity opens up interesting possibilities for the manufacture of food packaging. The most recent works actually study maize zein plastification by alcohols or fatty acids (73; 74). The purpose of this research is to obtain hydrophobic films whose cohesion would be ensured essentially by non-polar interactions (Van der Waals and hydrophobic), the polar groups then being pushed towards the heart of the protein structure. The manufacture of these films is then done by extrusion or thermo-forming.

1-3-4- Casein

Casein is the main protein in milk : one litre contains about 25 to 27 g of casein (75). Industrially, casein can be found in various forms : insoluble casein, particle calcium salts or entirely soluble sodium or potassium caseinates (76).

In the area of materials, it is found as the majority component of a composition aimed at the manufacture of flower pots (77) and often in association with lignins (78). Caseinates can also be polymerized by gamma radiations, by creation of bityrosine covalent bonds (79).

Other biopolymers

The extraction and use of starch and proteins, which are reserve elements of living cells, have been studied largely for their « plastic » properties. But other structure biopolymers can be used too.

1-4-1- Parietal polysaccharides

Native cellulose does not have thermoplastic properties (see 3-2), unlike all the other polymers which ensure cohesion of parietal structures. Their properties of texturation in water have been studied above all in the area of paper manufacture.

Cellulose

Cellulose fibers can be used to manufacture films. The plastic properties are obtained by a mechanical treatment. This treatment makes it possible to defibrillate the fibers : their organization is thus destroyed giving way to a tangle of microfibrils which are less complex and have a smaller diameter (80; 81). The individualized fibrils can then be made into a film by casting. These films therefore have interesting mechanical properties, all the more since the amount of polymers ensuring naturally the cohesion of fibers, such as pectins in the case of sugar beet, is great (82).

Pectins

The pectin substances present in various proportions in most higher plants play the role of inter-cellular cement, and contribute to the cohesion of vegetable tissues. Pectins are polysaccharides whose main skeleton is made up of a linear linking of α-D-galacturonic (1-4) acid units interrupted by alternating L-rhamnopyranose units, able to undergo a 90° deviation from the main axis of the pectin chain (83). The acidic functions of the galacturonic groups can be esterified by methanol. The physico-chemical properties of pectins and in particular gelatinisation depend on the degree of their methylesterification. The pectin chains can organize themselves in an aqueous medium and texture this medium, directly amongst themselves when their degree of methylation is above 50% or through divalent cations when their degree of methylation is weak (84).

These gelling properties allow the formation of a coating film by water evaporation. The first applications are old and concern the coating of fruits and dried vegetables to protect them from air humidity (85; 86). The insolubility of the complexes which the pectins form with calcium or other divalent cations (87) also makes it possible to cause their coagulation for fiber manufacture (88), and the incorporation of glycerol allows the films to acquire sufficient flexibility (table1). Moreover, like gelatine, pectins have a strong adhesive character (89). Finally, the anionic character of the acid functions of pectins is also used to form coherent materials by complexation with chitosan, the only cationic polysaccharide (90).

Fishman and Coffin also studied the thermal and structural properties of pectins, and their compatibility with polyvinyl alcohol (91). Films extruded from a pectin-starch mixture are thus obtained (92).

Hemicelluloses

Hemicelluloses are non-cellulose and non-pectic parietal polysaccharides which are extracted in an alkaline medium. This family includes a great variety of structures, and apart from the paper industry, relatively few works have been devoted to their exploitation as basis for materials. However, their rheological properties in solution in water have made it possible to obtain plastic films by casting, in the case of sorghum, of kenaf, of maize(93), of wheatbran (94) or of poplar tree (95) .

Other polysaccharides

Alginates are colloids issued from algae, they are used in the food processing industry for their texturing properties (96). A sodium alginate based composition intended for the manufacture of packaging has been proposed (97).

1-4-2- Lignin

Lignin acts as a reinforcement and a protection for the constituent fibers of the vegetable structure. Although the conformations and configurations of the lignin composites in liquid state and in solid state are not yet completely defined, the physico-chemical properties of these polymers of phenyl-propane type have been studied for over 20 years for applications in the area of materials (98). The stakes are high since a very small proportion of the lignin waste of the paper industry is valued.

Lignin derivatives are made up of lamellar macromolecular complexes inside which the polymers are strongly linked by many non-covalent molecular interactions, of which some are strong hydrophobic interactions between the aromatic nuclei (99). These internal intermolecular properties permit to envisage the synthesis of lignin-based plastic materials. Modified lignins have already been incorporated (100; 101) or grafted (102) with success in traditional thermoplastics and a composite containing 85% non-modified Kraft lignin has been developed. The ligneous residues of paper mill comprise very polar functions and an hydrophobic skeleton, their « plastic » properties are consequently not closely linked to the presence of a polar plasticizer such as water, but they can be added to starch (103). Lignins therefore constitute a composite of choice for the conception of biodegradable materials (table2). And they are found in the compositions of Napac® (104), of Protol® (77) and of Lignopol® (78). They are also used in the manufacture of injection granules after treatment with acid (78), which causes a partial depolymerization and improves in this way the plasticity of the material (99), or chemical reticulation (64).

2- CHARGES

All these biopolymers have interesting “plastic properties”, but the price of pure extract -1 kilogramm of thermoplastic starch costs for example about 1€- and the average mechanical resistance lead the researchers to add them charges, notably for the moulding of biodegradable objects. The composition of these composite materials get so close to that of natural matter, which can be considered as a complex macromolecular structure in which each constituent has a specific role. The parietal fibers of lignocellulosic type form the framework of the assembly and give it mechanical resistance (table2), and the amorphous components play the role of the matrix. But the conception of agro-materials is also based on the knowledge of the traditional plastic material industry. The use of mineral charges becomes thus widespread. The relationships between vegetable matter and minerals are actually naturally close and they often bring improvements in the properties of the materials other than a simple increase in their resistance.

Vegetable fibers

Vegetable fibers have been used since the beginning of the century to reinforce thermosetting resins. Although they later gave way to glass fibers, the present constraints of recycling materials has put them back at the forefront, also because of the mechanical properties comparable to those of synthetic fibers (table 3).

The three main constituents of these types of fibers are cellulose (60 - 80%), hemicelluloses (13 - 23%) and lignin (1 - 20%). Cellulose is a linear homopolymer of anhydroglucose units linked in β-1,4. The presence of free hydroxyls functions (3 per pattern) establishes many hydrogen links and leads to the formation of an orderly semi-crystalline structure. Cellulose is thus insoluble in most solvents and notably in water (105). Hemicelluloses are polysaccharides with ramified structures which play a first role of fibers binder by bringing a certain flexibility to the structure of cellulose microfibrils, but also ensure the compatibility phase with lignin. So the characteristic properties of natural fibers vary according to the proportions of these three polymers and therefore according to the plant part from which they are extracted (leaves or stalks), to the place of cultivation and to the age of the plant (6).

The first criteria for choosing a reinforcement fiber is its mechanical resistance which is directly related to the degree of polymerisation of the cellulose. But other criteria can also be important, such as their humidity, usually between 8 and 13%, or the quantity of wax which naturally covers them. The first influences the processing which always occurs at high temperature and the second conditions the wettability of the fibers and plays a preponderant role in the cohesion of the composite.

The area of fiberboards is of course the first consumer of fibers. Recent works concerning biodegradable resins and the use of fibers coming from agricultural production (106) will perhaps turn them into common agro-materials. But the area which seems to be the most advanced is that of thermo-moulded composites: light materials charged with long fibers whose non-isotropic properties are suited to the uses. In this way, the automobile industry finances a great deal of research in the selection of fibers (46) and the use of a biodegradable matrix (107).

Vegetable fibers are also used to reinforce biodegradable compositions intended to be processed like plastics. Cellulosic fibers in a starch matrix enhances the mechanical properties by direct reinforcement but through the increase of the glass transition temperature too (108) and decrease the water sensibility of the material (109; 110). Wood fibers are therefore present in the compositions of Treeplast® (111) or in those of materials of Bayer (112) or of Master (113) and chinese reed fibers in Napac® (104) or to make smart cards (114). Furthermore, certain authors use fibers with specific properties : long fibers to improve mechanical resistance and cover the pores of the matrix (115; 116), or cellulose microfibrils (110; 117; 118). And their surface can be modified to enhance their compatibility with a hydrophobic matrix (119; 120).

Finally, the fibers of the starch-containing plant can be used to form directly by extrusion a composite material moldable by injection, as it is in Vegemat® (121) with whole maize plant.

The use of agricultural waste or co-products

The food processing industry produces a large amount of waste and co-products rich in fibers, such as oil or sugar extraction residues, or simply maize or wheat stalks. The first are often used for animal food, while the second are presently of little use. However, their high cellulose content could be used to strengthen agro-materials (table 4), and especially because they are cheap.

In this way, there are many sources of fibers. Their availability depends on regional agricultural productions and on the commitment of agricultural cooperatives in favour of agro-materials. The used papers also constitute a large potential source of cellulose fibers.

Finally, certain residues contain biopolymers which can be used as a composite matrix. For example, a waste of agricultural origin such as sugar beet pulp can be directly processed after acid treatment which causes a slight depolymerization (122). The native structure is then transformed in a simple matrix/fibers structure. An enzymatic treatment of potato pulp leads to the same result (123). More recently a composition of which the main composite is beer brewing residue has been also proposed (124). In the same way, the plastic properties of globular proteins can be used to transform an extraction residue such as sunflower oil cake by thermo-molding (68) or by injection-molding (125; 126).

Mineral charges

The plastic industry uses many mineral charges to strengthen plastics : glass fibers, silica, talc… These charges are naturally employed in certain biodegradable compositions, but then they can have other function than simply improving mechanical resistance. Most biopolymers can interact with mineral matter, usually in the form of a complexation (see 3-1-3), which improves the quality of materials. The water retention properties of mineral composites can also limit the hydration of the vegetable matrix in a humid medium (127).

The salts used to strengthen the structure, to improve the hardness of materials (128) by filling in the matrix pores (129) are Zirconium salts (130) and the calcium salts, $CaCO_3$ (77; 131), $Ca(PO_4)_2$ (62), $Ca(OH)_2$ (132). Titanium oxide TiO_2 is also used in the composition of Maucourt (131) as a photochemical degradation agent. Raw minerals such as lime, gypsum, kaolin, talc or sand are also proposed (133; 134) to reduce the cost of the raw material. Kaolin is particularly interesting because of its surface polar residues which ensure the compatibility with an hydrophilic matrix like starch (135).

BIODEGRADABILITY AND DURABILITY

All the biopolymers which have been presented have hydrophilic functions, mostly hydroxyls or amines. Their capability to fix water with hydrogen bonds makes the materials formed sensitive to humidity but also makes them deteriorate easily. Indeed, the swelling of the polymeric network by the penetration of water allows micro-organisms to enter. Agro-materials are therefore mostly hydro-biodegradable.

But this essential property is also a weakness for a common use of these materials. That is why a lot of research is devoted to the improvement of their durability. It explores various means such as surface treatment or modification of the internal structure of the matter, by chemical or physical treatment, or simply by formulation.

Formulation

3-1-1- Lipids

Fat (oils, grease, wax...) is the most widespread hydrophobic raw material of natural origin. Its chemistry is actually in full expansion and the physico-chemical properties of their long carbon chains can be used in many applications : biofuels, biolubricants, tensioactives...

Lipids can therefore be employed to improve the properties of agro–materials, through various means.

The first is simply linked to the hydrophobic character of vegetable oils or of natural waxes (136). They are added to biodegradable compositions to act as lubricants or even as demoulding agents (61) while limiting the water exchanges with atmosphere (137). Water absorption in humid climatic conditions brings about deformations of the moulded pieces if they are not treated. But the flowing properties of the matter and its cohesion for the forming being conditioned by the hydrogen links of the biopolymer-plasticizer mixture, the quantity of oil added cannot be above 1 to 2% (137), except if they are hydroxylated (123; 128), if the mixture contains compatibilizing products, or if it is the fibrous components which are impregnated with it and which delay the outflow of oil (111).

But for agro-materials, vegetable oils are usually used for surface treatment. In that case, two properties are used to form a homogeneous protection. The first is solidification of hydrogenated oils at ambient temperature (130; 138) : by soaking a piece in heated oil and then cooling it, a protective layer is formed at the surface. The second, more interesting, is natural siccativity of unsaturated oils. In this case, linseed oil or castor oil for example can form hydrophobic plastic films, by radical oxidation reaction (139; 140). This property, which has been used since the 13th century by painters (141), is today commonly exploited for wood protection. This type of surface treatment can therefore also be employed to improve the durability of agro-materials (142) for example to manufacture paper mulch (143).

Epoxidized oils can also form resins (143; 144), which can then be used as majority compound of a composition containing dry starch and fibers (113). But the possibilities of polymerisation of natural oils are for the most part developed to form directly plastic materials (145). Siccativity is then no longer sufficient (the resins turn yellow and the ether bridges formed are not strong enough). The reticulation is then obtained by chemical means by reaction between polyisocyanates or aldehydes and the hydroxylated fatty chains, like those of castor oil (146), by cationic polymerisation of high unsaturated glycerides (147) or by using the properties of the phenolic nuclei contained in cashew nut shell liquid (148). The latter is actually particularly interesting because it contains unsaturated fatty chains, and so it has siccativity properties too (149).

3-1-2- Hydrophobic polymers

Natural hydrophobic polymers

Nature also created hydrophobic structures, whose degradation is ensured by photochemical processes. They can therefore be used to improve the durability of agro-materials while preserving their biodegradability.

The most known of these polymers is natural latex. It is used in mixture in certain compositions (97; 150), where, in addition, it helps to improve the flexibility of the moulded objects (151) or in surface treatment (152). But the applications remain limited due to its high cost.

Another type of polymer is more often employed : natural resins. This generic term includes a wide variety of reticulate polymers, which are the secretion products of many vegetables. Gums (Dammar, Kopal) or rosins (of resin, wood or Tall-oil), they are used for their double affinity with polymers of vegetable structures and with fat (111; 128) or hydrophobic polymers (153). They thus ensure good cohesion between a piece and its hydrophobic coating (130). This adhesive character which can cause the materials to be sticky can be tempered by adding wax to the mixture (153).

Synthetic polymers

Introduced in the 80´s, the biodegradable synthetic polymers developed by big industrial groups -BASF, Solvay, Bayer, DuPont, Monsanto, Cargill- are today in the industrialization phase (6). They are often used in biodegradable compositions with biopolymers (154), sometimes to improve their properties, but often the purpose of the mixture is only to reduce the cost of the raw material, as these plastics, although possessing interesting properties, are still very expensive.

The use of hydrophobic polymers brings about problems of compatibility with hydrophilic biopolymers. These problems can be resolved by using compatibilizing agents such as natural resins (153; 155), siloxanes or silanes (119; 156; 157), or copolymers of which certain monomeric units are polar (158), by chemical modification of the polymers (159), or by reticulation of the mixture components.

The polymers used are essentially polyvinyl alcohol or polyvinyl acetate (50; 91; 160), polycaprolactones (161), polylactic acid (162; 163) or are only described as linear polyesters (49; 112; 164; 165; 166). They are usually used in bulk, but a surface treatment is also considered in certain works (155; 167; 168). Certain fluoride polymers, hydrophobic and lipophobic, are also used (169).

3-1-3- Minerals

Minerals are used in different ways to improve the properties of agro-materials. First of all, the biopolymers which have acid functions (susceptible of being put in anionic form) can form complexes with divalent cations. The example of pectins (87; 88; 170) is common as their jellification has been greatly studied. But this property has also been used with wheat gluten (67). The result is always an increase in the fragility of the material (breaking stress and modulus increase while deformation decreases) and a net decrease in its water solubility (table1). The ionic interactions generated are sufficiently strong to prevent water from penetrating into the network. Similar results can be obtained by complexation with tannins if the structure of the biopolymers is compatible (171), but then the involved interactions are hydrophobic (172). Minerals can also cause new interactions to appear; for example treating fibers with alum allows the creation of anionic absorption sites (115).

Minerals also have an influence on the relationship between the plasticizer (solvent) and the biopolymers. The influence of ions on the stability of proteins has often been studied in this respect (42). The minerals displace and fix the hydration water of the polymers, thus causing a tightening of the chains and establishing new polymer-polymer interactions. This property can then be used to improve the durability of agro-materials by immersing pieces in a saline solution or by adding minerals to the mass (127).

Finally, certain composites of mineral origin are hydrophobic and can directly improve the water resistance of biodegradable compositions: this is the case of potassium siliconate (132) and of some polyphosphate, whose plastic properties increase the quantity of admissible charge (173). In a mixture with soybean proteins and starch, and following a siloxane compatibilization treatment, it is possible with those polyphosphates to halve the water absorption of the material (61).

Chemical modification

Chemical modification, which brings about the formation of covalent bonds, allows to change the properties of biopolymers. In a pure state the modified polymers have serious industrial outlet, but then it exceeds the scope of agro-materials. The classic example of cellulose is representative of this. In its native state, cellulose has no thermoplastic property. But an esterification reaction of the hydroxyl groups with acids makes it acquire new properties of flow, of resistance and of durability comparable to those of a synthetic plastic**.** Chemical grafting of biopolymers is therefore one of two means which can be employed to obtain more resistant materials, the other being reticulation. By forming covalent links between the chains from the hydrophilic functions, the hydration possibilities and the flowing properties diminish, while the cohesion of the system becomes stronger. However, although these methods really do make it possible to markedly improve the durability of materials, it is often to the detriment of their biodegradability (174; 175).

3-2-1- Grafting

Esterification of the hydrophilic functions of starch (176; 177) and of cellulose (178; 179) can form polymers of which the physico-chemical properties are suitable for the manufacture of materials. It causes an internal plastification of the polymers, the lateral groups increase the volume available inside the network and give to the chains a greater mobility and this increases the water resistance of the material by decreasing the quantity of free hydroxyl functions. Depending on the nature and quantity of the grafted groups, the properties obtained can be completely different: an acetyl group improves plasticity, while a fatty chain brings a pronounced hydrophobic character.

Modified starch is thus often used in mixtures with native starch to improve the water resistance of the finished materials (180; 181) or as the only composite of the matrix (118; 182). The same goes for cellulose acetate (183).

But the described chemical grafting has a major disadvantage linked to the operating conditions of the reactions to be employed : the use of acyl halogens require a solvent medium and the use of acids necessitate high temperatures which partly damages the biopolymers. And so softer conditions are now developed with hydroxyalkenyl acids and a catalysor (184), or mixing of anhydrides and epoxydes (185) and if it is possible by extrusion process (186).

3-2-2- Reticulation

Reticulation consists in linking together two hydrophilic nucleophilic functions by using a polyfunctional agent. There are many works in this area. The use of dialdehydes on starch (187) or on proteins (188; 189; 190) is the most common method. It makes it possible to improve resistance and to reduce the solubility of films (191). Unfortunately, all the short-chain dialdehydes are toxic (192). The use of polyepoxydes presents the same problems and that of polyacids requires harsher reaction conditions. Attention is therefore turned to acrylic (193) or vinyl (194) derivatives, for which the reticulation reaction occurs in mild conditions (195).

Two other non-toxic reticulation methods are employed via the chemical modification of starch. An oxidation makes it possible to create DAS (dialdehyde starch), which can then react directly with the amine functions of proteins for example (196). And the use of starch polyphosphates finds new applications (197) fourty years after their discovery (198).

3-3- Thermal treatment

Controlled thermal treatment of agro-materials can also improve their durability. The challenge is then to eliminate the water of constitution of the material while preserving sufficient mobility in the chains, at a temperature higher than the glass transition temperature of the mixture, so that they can interact amongst themselves (199) : covalent links can even be formed by radical reactions (200). Water evaporation becomes then irreversible. The consequences of the treatment are therefore an improvement in the durability of the material accompanied by an increase in its fragility (table1).

This treatment is used for the protection of wood (199) and has been tried on proteic films (193; 201; 202).

CONCLUSIONS AND PERSPECTIVES

The results of the works published amply show that it is possible to manufacture materials from biopolymers issued from renewable raw material :

- Highly hydrophilic biopolymers, such as starch (34) or gelatine (16), when plastified can be processed by injection-molding ;
- Less soluble biopolymers, such as lignins (99) or proteins (44) can be used as resins. They are therefore susceptible to be formed by thermo-moulding or used to increase the durability of polysaccharide-based compositions ;
- The use of an organic plasticizer makes it possible to manufacture compounds which are ready for use and preservable (111) and to decrease the fragility of agro-materials;
- In formulation, vegetable oils, minerals or hydrophobic polymers can greatly improve the durability of the materials while preserving their biodegradability (33);
- Chemical modification through reticulation and grafting completely modify the properties of biopolymers.

Since the mechanical resistances obtained are comparable to those of traditional synthetic plastics such as PE or PP, these materials are suitable for many applications, for which water impermeability is not essential. This weakness remains the main limit to their being used, particularly in the face of biodegradable synthetic plastics. Nevertheless it must be emphasized that these degrade only in specific composting conditions and their use requires the sorting out of waste (203).

Another restriction on the mass development of these materials, remains their cost. By using purified extracts such as starch and by formulating complex compositions, for productions of low tonnage, the price cannot be competitive when compared to petrochemical plastics. One perspective to reduce costs is therefore to use raw vegetable matters.

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Composition	Solution/treatment	Test conditions	Tensile strength (Mpa)	Elongation (%)	Reference
Starch/water (9/1)	Water/85-90 °C 15 min	-	50.5 ± 5.4	4.2 ± 0.5	Arvanitoyannis, 1999
Starch/MC/water (4.5/4.5/1)	Water/85-90 °C 15 min	-	61.2 ± 6.5	8.9 ± 0.9	Arvanitoyannis, 1999
Starch/MC/glycerol/water (4/4/1.5/0.5)	Water/85-90 °C 15 min	-	43.3 ± 5.0	25.3 ± 1.9	Arvanitoyannis, 1999
Starch/MC/sorbitol/water (4/4.1.5/0.5)	Water/85-90 °C 15 min	-	35.2 ± 2.0	28.7 ± 2.4	Arvanitoyannis, 1999
Starch/MC/xylose/water(4/4.1.5/0.5)	Water/85-90 °C 15 min	-	32.5 ± 3.0	21.5 ± 2.3	Arvanitoyannis, 1999
SPI/glycerol (5/3)	pH=8/ 13 °C 15h	25°C-50% RH	4.33	78.2	Brandenburg, 1993
SPI/glycerol (5/3)	pH=10/ 13 °C 15h	25°C-50% RH	5.23	90.3	Brandenburg, 1993
SPI/glycerol (5/3)	pH=12/ 13 °C 15h	25°C-50% RH	4.54	85.6	Brandenburg, 1993
SPITS/glycerol (5/3)	pH=8/ 13 °C 15h	25°C-50% RH	3.74	111.9	Brandenburg, 1993
SPITS/glycerol (5/3)	pH=10/ 13 °C 15h	25°C-50% RH	4.33	115.2	Brandenburg, 1993
SPITS/glycerol (5/3)	pH=12/ 13 °C 15h	25°C-50% RH	3.95	107.3	Brandenburg, 1993
SPITT/glycerol (5/3)	PH=11/ 70°C 30 min/ 95°C 2h	25°C-50% RH	7 ± 0.5	75 ± 10	Gennadios, 1996
SPITT/glycerol (5/3)	PH=11/ 70°C 30 min/ 95°C 24h	25°C-50% RH	14 ± 2	25 ± 10	Gennadios, 1996
SPITT/glycerol (5/3)	PH=11/ 70°C 30 min/ 80°C 24h	25°C-50% RH	10 ± 1.5	30 ± 10	Gennadios, 1996
SPI 7S/glycerol (5/1.5)	PH=10/ 25°C 15h	25°C-50% RH	7.36 ± 0.42	8.6 ± 0.2	Kunte, 1997
SPI 11S/glycerol (5/1.5)	PH=10/ 25°C 15h	25°C-50% RH	10.7 ± 0.6	4.0 ± 0.05	Kunte, 1997
SPI/glycerol (2/1)	PH=10/ 70°C 20 min	25°C-50% RH	6.3 ± 0.2	66 ± 25	Rhim, 1998
SPI/glycerol/DAS (2/1/0.2)	PH=10/ 70°C 20 min	25°C-50% RH	6.2 ± 0.6	53.3 ± 1.2	Rhim, 1998
SPI/water/glycerol (10/8/3)	Extruded 120-160°C output 0.35-1.5 mm	50% RH	14.3 ± 0.5	119 ± 12	Zhang, 2001
SPI/water/glycerol/$ZnSO_4$ (10/8/3/2)	Extruded 120-160°C output 0.35-1.5 mm	50% RH	16.7 ± 0.8	131 ± 14	Zhang, 2001
SPI/water/glycerol/ECH (10/8/3/0.4)	Extruded 120-160°C output 0.35-1.5 mm	50% RH	16.9 ± 0.9	162 ± 15	Zhang, 2001
SPI/water/glycerol /GA(10/8/3/0.4)	Extruded 120-160°C output 0.35-1.5 mm	50% RH	15.8 ± 1.2	146 ± 8	Zhang, 2001
SFP/glycerol (0.00545mol/g)	PH=12/ 25°C 25h	25°C-60% RH	3.9	250	Ayhllon, 2000
SFP/sorbitol (0.00545mol/g)	PH=12/ 25°C 25h	25°C-60% RH	4.5	85	Ayhllon, 2000
SFP/glycerol (0.00545mol/g)	Thermopressed 155 °C	25°C-60% RH	7 ± 0.4	92 ± 6	Ayhllon, 2000
SFP/1,3 propanediol (0.00545mol/g)	Thermopressed 155 °C	25°C-60% RH	10 ± 0.7	43 ± 2	Ayhllon, 2000
Maize zein/oleic acid (2/1)	Ethanol/ 25 °C 24h	25°C-50% RH	8.7 ± 1.0	11.9 ± 3.1	Lai, 1998
Maize zein/oleic acid (2/1)	Ethanol/ 25 °C 24h	25°C-98% RH	8.0 ± 1.4	28.4 ± 12.4	Lai, 1998
Maize zein/oleic acid (2/1)	Isopropanol / thermopressed 150 °C	25°C-50% RH	9.4 ± 0.8	5.9 ± 2.4	Santosa, 1999
Maize zein/oleic acid (10/7)	Isopropanol / thermopressed 150 °C	25°C-50% RH	4.2 ± 0.5	47 ± 24	Santosa, 1999
Maize zein/oleic acid (1/1)	Isopropanol / thermopressed 150 °C	25°C-50% RH	2.2 ± 0.3	7.5 ± 1.5	Santosa, 1999
Maize gluten/glycerol (4/1)	Brabender 80 °C / thermopressed 110 °C	25°C-60% RH	4.3 ± 0.2	1.1 ± 0.1	Di Gioia, 1998b
Maize gluten/octanoic acid (4/1)	Brabender 80 °C / thermopressed 110 °C	25°C-60% RH	16.4 ± 1.6	1.7 ± 0.3	Di Gioia, 1998b
Wheat gluten/glycerol (2.7/1)	52% EtOH pH = 2-4/ 75 °C 10 min	25°C-50% RH	0.5-0.9	157-229	Gennadios, 1993a
Wheat gluten/glycerol (2.7/1)	52% EtOH pH = 9-13 /75 °C 10 min	25°C-50% RH	1.9-4.4	170-208	Gennadios, 1993a
Wheat gluten/glycerol (2.5/1)	52% EtOH /75 °C 10 min	25°C-50% RH	2.6	238-276	Gennadios, 1993b
Wheat gluten/glycerol (2.5/1)	52% EtOH /75 °C 10 min/lactic	25°C-50% RH	1.4	417	Gennadios, 1993b
Wheat gluten/glycerol (2.5/1)	52% EtOH/75 °C 10 min /$CaCl_2$	25°C-50% RH	3.8	162	Gennadios, 1993b
Wheat gluten(SST)/glycerol (4.3/1)	32% EtOH/ 50°C/ 80°C 15 min	20°C-60% RH	2.4 ± 0.4	391 ± 58	Micard, 2000
Wheat gluten(SST)/glycerol (4.3/1)	32% EtOH/ 50°C/ 110°C 15 min	20°C-60% RH	3.1 ± 0.4	327 ± 58	Micard, 2000
Wheat gluten(SST)/glycerol (4.3/1)	32% EtOH/ 50°C/ 140°C 15 min	20°C-60% RH	7.3 ± 1.2	170 ± 26	Micard, 2000
Wheat gluten(SST)/glycerol (4.3/1)	32% EtOH/ 50°C/ formaldehyde vapor	20°C-60% RH	8.1 ± 0.8	190 ± 27	Micard, 2000
Casein/glycerol (5.7/1)	Water/ 90 °C 30 min	25°C-50% RH	29.1	4.1	Mc Hugh, 1994
Casein/glycerol (2.3/1)	Water/ 90 °C 30 min	25°C-50% RH	13.9	30.8	Mc Hugh, 1994
Casein/sorbitol (2.3/1)	Water/ 90 °C 30 min	25°C-50% RH	14.0	1.6	Mc Hugh, 1994
Casein/glycerol (1.5/1)	Water/ 90 °C 30 min	25°C-50% RH	18.2	5.0	Mc Hugh, 1994
Pectin (DE=32%) glycerol (1.5/0.6)	EtOH-water/ 55 °C 4 h dryer	25°C-50% RH	14.1	8.7	Pavlath, 1999
Pectin (DE=32%) glycerol (1.5/0.6)	Eth-water/ 55 °C 4h/5min sol Ca^{2+} at 5%	25°C-50% RH	52.9	2.1	Pavlath, 1999
Starch/Cas/glycerol/Lec (7/3/6/0.2)	Extruded 100 °C output 0.1 mm	45% RH	1.7	20	Nakatsuka, 1978
Starch/Cas/glycerol/Lec (7/3/6/0.2)	Extruded 100 °C output 0.1 mm	65% RH	0.8	35	Nakatsuka, 1978
Starch/Cas/glycerol/Lec (5/5/3/1)	Extruded 100 °C output 0.1 mm	45% RH	1.8	70	Nakatsuka, 1978
PEBD		-	9-17	500	Briston, 1986
PVC		-	45-55	120	Briston, 1986
PET		-	175	70-100	Briston, 1986
Cellophane		-	48-110	15-25	Briston, 1986

MC: Metyl-cellulose - NACAS: Sodium caseinate - SPI: Soybean protein isolate - Lec: Lecithin - SPITS: Soybean protein isolate treated with soda – SFP: Sunflower protein -SPITT: Soybean protein isolate thermally treated – SST : sodium sulfite treated – ECH : epichlorhydrin – GA : glutaric dialdehyde

Table 1. Comparison of the mechanical properties of biopolymers films.

Composition	Moulding				Deformation (%)	Reference

Fiber	Tensile strength (Mpa)	Young ‘s modulus (Gpa)	Elongation (%)	Fiber	Tensile strength (Mpa)	Young’s modulus (Gpa)	Elongation (%)
Cotton	287-800	5.5-12.6	7.0-8.0	Pineapple	413-1627	34.5-82.5	1.6
Jute	393-773	13-26.5	1.16-1.5	Leather	131-175	4-6	15-40
Flax	345-1100	27.6	2.7-3.2	Glass-E	2000-3500	70	2.5
Hemp	400-938	61.4-128	1.2-3.8	Glass-S	4570	86	2.8
Ramie	400-938	61.4-128	1.2-3.8	Aramid	3000-3150	63-67	3.3-3.7
Sisal	468-640	9.4-223.0	3-7	Carbon	4000	230-240	1.4-1.8

Table 3. Comparison of the mechanical resistance of various natural and synthetic fibers (Mohanty, 2000b).

Grain residue issued from beer brewing, from the fabrication of sake or from spirit distillation.	Andou, 1998
Wheat bran.	Rigal, 1998a
By-products of the treatment of lucerne.	Fouad, 1998
Sugar beet pulp.	Turbaux, 1997; Baar, 1997; Rigal, 1995
Wheat straw.	Gonod, 1997; Markessini, 1997; Rigal, 1998b
Potato skins.	Jongboom, 1999
Oleaginous oil-cakes (oil extraction residue).	Baganz, 1999; Silvestre, 2000; Rigal, 2000
Rye, oats.	Thobor, 1996
Old paper waste.	Van Delft, 1994; Baar, 1997; Nakamura, 1999; Morgan, 2000
Coconut fiber powder.	Sugimoto, 2000; Belger, 2000

Table 4. Use of agricultural waste or co-products in agro-materials.