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Properties and Biodegradation Nature of Thermoplastic Starch

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1. Introduction

For the last few decades, the usage of plastic increased because of its specific properties such as low cost, light weight, high strength, non-biodegradability, durability, non corrosive nature, process ability and high energy effectiveness. Hence these plastics can be used for various application which includes household articles to aeronautic sector. Now a day it's difficult to imagine a life without plastic which are mostly derived from crude oils and natural gas. Among the various polymers, polyethylene, polypropylene and polystyrene are used greatly for food packaging, biomedical field and in agriculture. According to statistics, from 1950 onwards, 9% of growth can be seen globally, in the production and consumption of plastics. In 1950 the overall production of plastic was 1.5 million tones while it reached 245 million tones in 2008.

In these polyethylene is one of the most dominant packaging material, creating the real problems in the disposal of one-trip packaging. These polymers will take millions of years to degrade under natural weathering conditions. Hence careless dumping of these plastics after its usage creates severe problems to the environment. Also during combustion it produces toxic materials which eventually pollute the atmosphere. The land filling results in the contamination of water, thereby adversely affecting the soil's biological balance. 'Recycling' is another solution for reducing the amount of waste polyolefin materials. But recycling has its own limitation in regard to compatibility of different polyolefins which adversely affects the processability and final properties. Subsequently the problems created by plastic wastages to the environment triggered the interest in the development of biodegradable disposable plastics. So that the onetime use items can be disposed off with the hope that they will not remain for centuries in a landfill, or as litter, which is one of the tenets driving the recent interest in "green" technologies. The current biodegradable plastics, such as PLA, PHBV, Mater-Bi etc are very costly and the processing and mechanical properties of these materials are not good enough for the production of consumer products. Hence several studies were conducted to modify the current commodity plastics such as

polyethylene, polypropylene into biodegradable type. One method to achieve this goal was blending of plastics with biodegradable agricultural feed stocks to meet the requirements of responsible and ecologically sound utilization of resources. This will reduce our dependence on depleting petrochemical resources.

2. Fabrication of thermoplastic starch

The fusion of mixture of native starch granules with sufficient amount of plasticizer, at lower temperature than their degradation, leads to a starchy material consisting of entangled polysaccharide chains. This material is called thermoplastic starch (TPS). Most common methods used for the preparation of TPS are extrusion and solvent casting method. For that various types of plasticizers such as glycerol, water, urea formamide etc are used during the formulation. The characteristics of mechanical work and flow (temperature, pressure, residence time, energy) during the preparation of TPS are known and modeled [Agassant et al., 1996, Vergnes et al., 1998]. A specific mechanical energy (SME) higher than 300kJ/g is necessary to achieve a complete destructure of starch granules. The presence of low molecular mass (plasticizers) raises the threshold energy similar to the action of sugars in the cereal products [Fan et al., 1996]. The SME transmitted as shear, leads to the breakdown of starch grains by fragmentation, and once the melt phase obtained, it is accompanied by a moderate depolymerization, particularly in the amylopectin [Barron et al., 2002].

The native starch can be transformed to TPS by several treatments which destroys its granular structure. Physical treatment requires simultaneous action of temperature, shear and lower water content during extrusion. Initially amorphous regions of starch granules are more accessible to water followed by its crystalline zones. The amount of water should be sufficient to hydrate these starch molecules which ultimately results in its gelatinization. Also for obtaining the melt phase of plasticized TPS, additional energy is required to destroy the residual crystalline structures. This mechanical treatment reduces the crystallinity of starch granules. Figure 1 shows that the viscosity of plasticized starch is of the same order and magnitude as those of synthetic thermoplastics at lower temperatures [Martin et al., 2003].

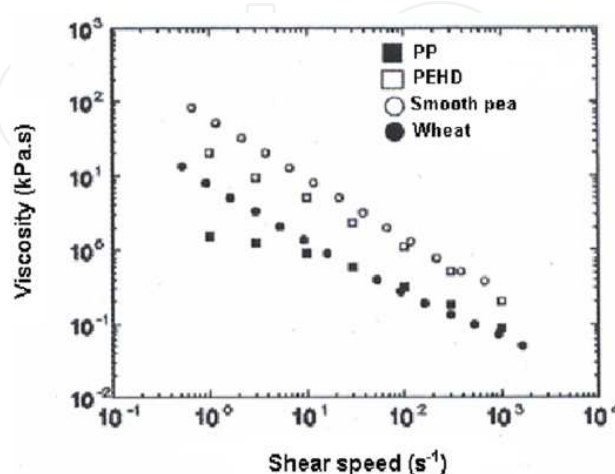


Fig. 1. Flow curves of thermoplastic materials at 200°C and TPS from smooth pea and wheat at 125°C

3. Properties of thermoplastic starch

3.1 Morphology

Studies show that the structures of native and thermoplastic wheat starch are totally different. Scanning Electron Micrograph (SEM) reveals that the native wheat starch has a granular structure (Figure 2) [Leblanc et al., 2008].

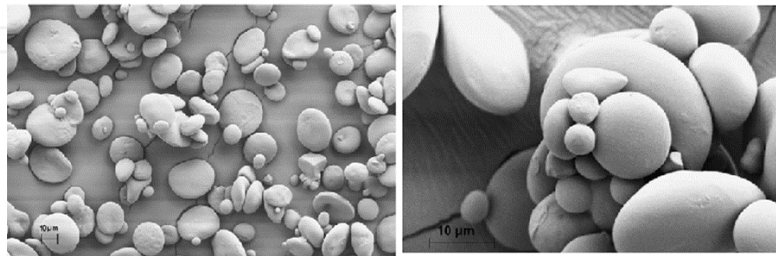


Fig. 2. SEM micrographs of native wheat starch

These granules are spherical or oval and have different domain sizes. They are smooth, free from pores, cracks, or fissure around to lenticular and polyhedral shapes and are relatively thick. For both starch granules there exists a wide distribution of granule size. This wide distribution is a common feature of cereal starch [Buleon et al., 1998; Charles et al., 2003]. During plasticization (the transformation of granular morphology into a homogeneous polymeric film), the destruction of hydrogen bonds between the starch molecules occurs synchronously with the formation of the hydrogen bonds between the plasticizer and starch molecules [Yang et al., 2006].

The extrusion method is a combination of thermal and mechanical input. During this process, starch was plasticized and a homogeneous molten phase characteristic of thermoplastic polymeric material was obtained (Figure 3) [Saiah et al., 2009].

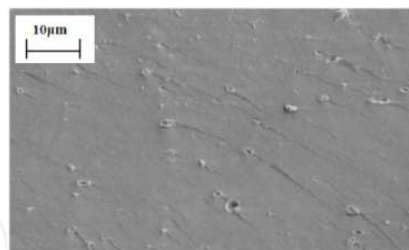


Fig. 3. SEM of extruded wheat starch based thermoplastic film

3.2 Structure

The X-ray diffraction (XRD) patterns for native and plasticized starch based on wheat flour (with 9% water and 12.8% glycerol) are displayed in Figures 4 A and B, respectively [Saiah et al., 2007]. The signal obtained from XRD, for native starch shows the semi-crystalline nature of this material. The diffraction peaks were obtained at 2θ values equal to 11.3, 15.2, 17.3, 18.1, 20.1, 23.3, and 26.7°, leading to the conclusion that these raw materials present A-type crystalline structure. This general characteristic of cereal starches was already observed in many other studies [Katz and Van Italie, 1930; Le Bail et al., 1993; Krogars et al., 2003]. For the extruded thermoplastic films, the peak appears at $2\theta = 7.2^\circ, 12.9^\circ, 19.8^\circ,$ and 22.6° (Figure

4 B); which are characteristics of a V_h -type structure [Le Bail, 1995; Fanta et al., 2002] indicating a change in the initial crystalline structure of native starch wheat flour. This structure was obtained by complexation of amylose with lipids. However, another peak at $2\theta = 17.3^\circ$ was observed which corresponds to an A-type structure. This A-type residual crystallinity is due to incomplete destruction and fusion during the transformation [Van Soest et al., 1996(c); Willett and Doane, 2002].

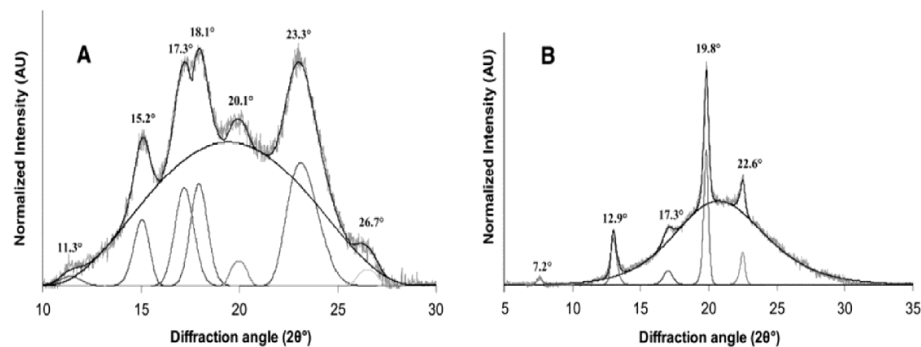


Fig. 4. XRD pattern of native (A) and extruded (B) wheat flour showing different contributions to rebuild experimental signals

The allomorph V_h (Figure 5) obtained with lipid unicycles and linear alcohols is the most common and most studied due to its involvement in many transformations of the starch. It is characterized by an orthorhombic lattice ($a = 1.37$ nm, $b = 2.37$ nm and $c = 0.805$ nm) and P212121 space group type.

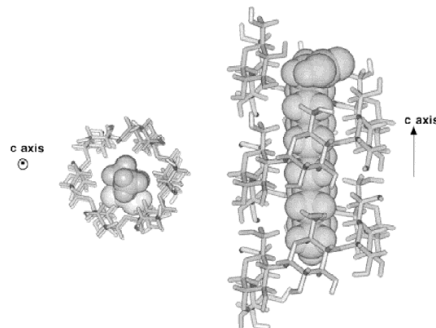


Fig. 5. Conformation of inclusion model of a fatty-acid in an amylose helix (Structure of V_h -type)

The V_a structure is another form of crystalline amylose-lipid complex. The characteristic angles of XRD peaks are respectively at $2\theta = 7.8$, 13.5 and 20.9° [Paris et al., 2001]. It is characterized by an orthorhombic lattice ($a = 1.30$ nm, $b = 2.25$ nm, $c = 0.79$ nm) with a P212121 space group [Winter and Sarko (a), 1974; Zaslow et al., 1974; Winter and Sarko (b), 1974]. In the V_a crystal structure, the helices of amylose are more contracted and there is less water compared to the V_h crystal structure. The transition V_h form to V_a is observed when the form V_h is dried to a water activity less than 0.6 [Rappenecker and Zugenmaier, 1981; Hinkle and Zobel, 1968; Murphy et al., 1975]. This transition is reversible because it is possible to transform the V_a type to V_h type by hydration in the vapor phase. It is usually interpreted as a change of form during the hydration with increasing distance between helices of 1.30 to 1.37 nm [Van Soest et al., 1996; Zaslow and Miller, 1961] due to the

introduction of water molecules between amylose helix. The V_a form is never obtained by direct crystallization of solutions of amylose, which is not the case of structures of type A, B and V_h [Buléon et al., 1984].

To have more information regarding the effect of plasticizers on the structure [Saiah et al., 2007], the amount of one plasticizer was kept constant (i.e., water initially fixed at 9%), and the percentage of glycerol varied from 12.8% to 16.5%, keeping the total amount as 20%. For all these materials, the same 2θ values peaks were observed and also the characteristics peaks for V_h and A-type crystalline structure. Also an increase in the intensity of the amorphous halo can be seen as a function of glycerol content (Figure 6).

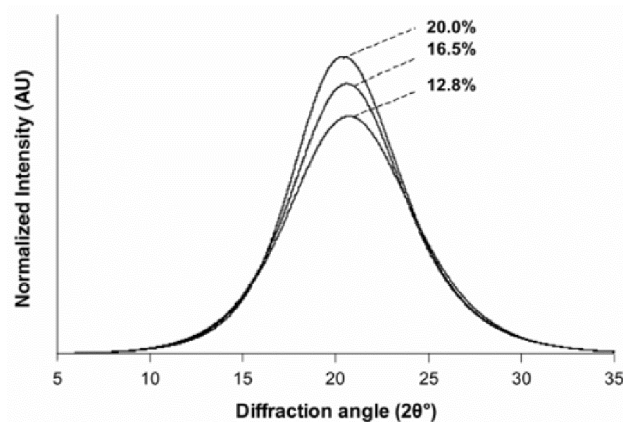


Fig. 6. XRD pattern showing variations in the amorphous halo as a function of glycerol content

In other words, the increase in percentage of glycerol decreases the percentage of crystallinity of the material from 14 to 11%. Table 1 gives the characteristics of the amorphous halo (the maximum diffraction angle, θ_m), which allows calculation of an average intermolecular distance (d_m) according to the Bragg formula (1):

$$2d_{hkl} \sin \theta = n\lambda \quad (1)$$

where λ is the wavelength of X-rays ($\lambda_{K\alpha Cu} = 1.54\text{\AA}$) and n is a positive whole number called order of diffraction.

Glycerol (%o, w/w)	θ_m	$\sin \theta_m$	$d_m (\text{\AA})$
12.8	10.36 ± 0.02	0.1798	4.28 ± 0.008
16.5	10.30 ± 0.02	0.1788	4.31 ± 0.008
20.0	10.20 ± 0.02	0.1770	4.35 ± 0.008

Table 1. Maximum diffraction angle and average intermolecular distance observed from XRD

The amorphous halo shifts toward the smaller angles when the percentage of glycerol increases, which increases the average distance between two molecular chains. The position of the amorphous halo reflects the average density (or specific volume) of the material [Arrighi et al., 1998]. When the average intermolecular distance increases from 4.28 to 4.35\AA , the average density (or the specific volume) decreases (Figure 7).

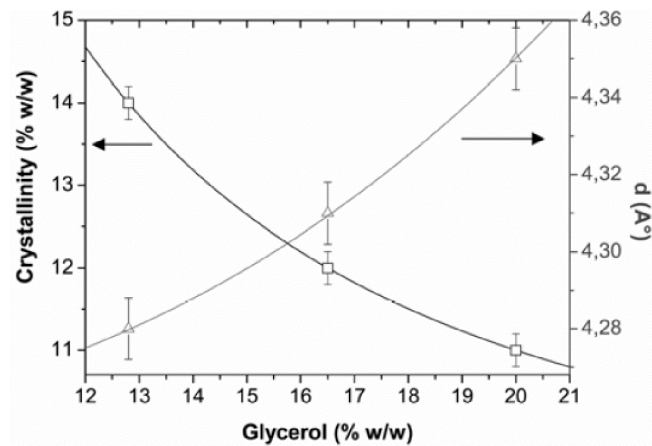


Fig. 7. Variations in crystalline fraction of samples and modification of average intermolecular distance in amorphous domains, when glycerol content changes

As a consequence, it is expected that the amount of free volume linked to existence of an amorphous or a vitreous phase increases in the extruded materials.

3.3 Mechanical behavior

The mechanical properties of TPS are influenced by the botanical origin of starch, more specifically the proportion of amylose and amylopectin. The materials obtained from wheat, corn and potatoes starch, have failure stress above that of a material based on waxy maize starch (rich on amylopectin) (Figure 8 a) [Hulleman et al., 1998]. Tensile tests on films of pure amylose and amylopectin highlights the difference in behavior between these two materials (Figure 8 b) [Lourdin et al., 1995]. The amylopectin based material has a ductile behavior (high failure strain), while that based on amylose has a typical behavior of a brittle material.

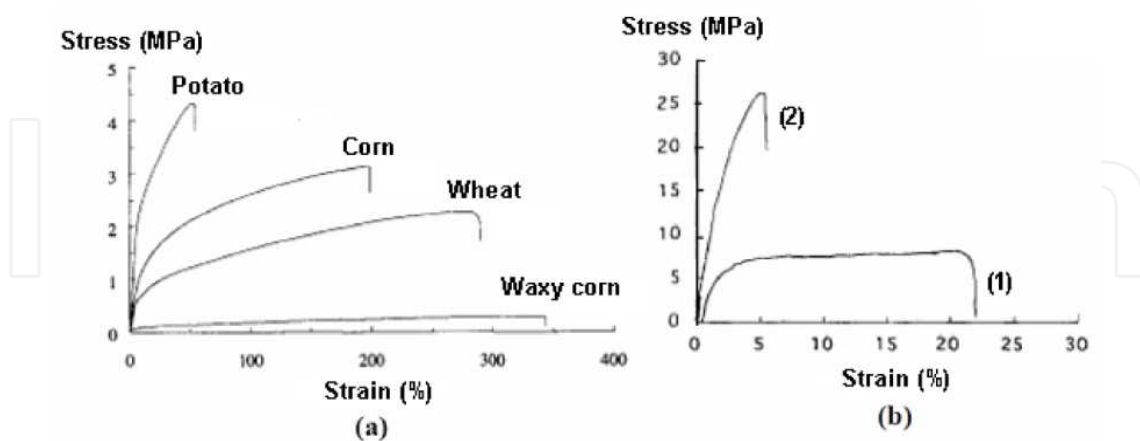


Fig. 8. Stress-strain curves for: (a) based materials starch potato, corn, wheat and waxy maize (b) materials based pure amylopectin (1) and pure amylose (2)

The effect of plasticizers on film resulting from agro-resources, generally leads to a decrease in the modulus and failure stress, and an increase in failure strain (Figure 9) [Poutanen and Forsell, 1996 ; Gontard and Guilbert, 1993; Lourdin et al., 1997].

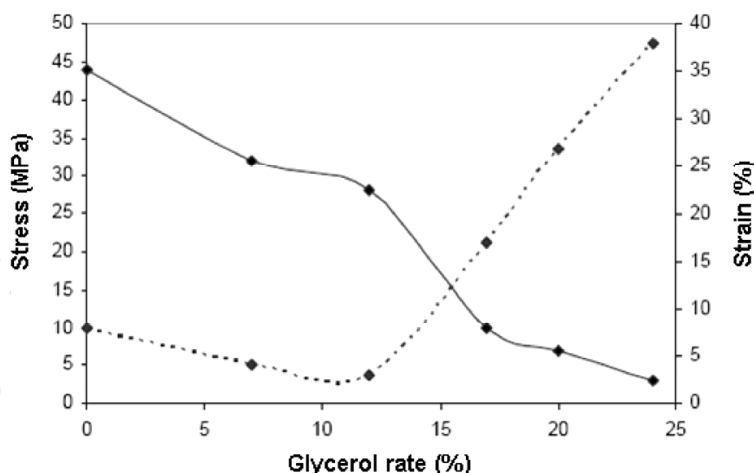


Fig. 9. Influence of glycerol rate on the strain at break (—) and stress at break (---) for potato starch films [Lourdin et al., 1997]

For glycerol level below 12%, a phenomenon “antiplastification” is observed, resulting in decreased stress and strain at break. This phenomenon is due to strong interactions between the polymer and the plasticizer, which forms a hydrogen network reinforcing material. From 12%, the strain at break increases quickly, against the stress at break decreases, and that up to 25% glycerol. This change in mechanical behavior is due to displacement of the glass transition temperature (T_g) of the system below the ambient temperature. The values of stress at failure, strain at failure, and tensile modulus are summarized in Table 2 [Saiah et al., 2007].

Glycerol (%)	σ_{max} (MPa)	ϵ_{max} (%)	E (MPa)
12.8	3.2 ± 0.10	17.0 ± 1.0	125 ± 6
16.5	2.7 ± 0.20	19.4 ± 1.2	102 ± 6
20.0	2.1 ± 0.12	22.9 ± 0.5	57 ± 4

Table 2. Tensile properties of wheat flour based TPS having different glycerol content

Adding glycerol during the formulation of TPS, decreases the stress at failure from 3.2 to 2.1 MPa and the tensile modulus from 125 to 57 MPa, while an increase from 17 to 22.9% in strain at failure. These results indicate that the ductility of material increases and, as expected, a plasticization effect is obtained by introducing glycerol in the sample composition. These plasticization effects due to glycerol have been observed in TPS made of starch from other sources [Mali et al., 2006]. In these introducing plasticizer reduces direct interaction between starch chains, thus facilitating movement of starch chains under tensile forces [Garcia et al., 1999; Mali et al., 2002]. The same scenario occurs for wheat-flour-based TPS.

Similar to glycerol, the addition of sorbitol will lead to a significant change in the mechanical behavior of TPS and antiplastification effect is also observed at sorbitol content less than 27% [Gaudin et al., 1999]. Beyond this amount sorbitol acts as a plasticizer in TPS. During the storage of films, changes in mechanical properties can occur [Van Soest and Knooren, 1997 ; Van Soest et al., 1996 (d); Forssell et al., 1999]. The strain at break decreases, while the stress at break increases. The changes observed over time are due to several concurrent factors: reduction in water content [Van Soest et al., 1996 (b); Van Soest et al.,

1996 (a)], increased T_g and crystallinity. Ageing causes reorientation and/or crystallization of molecules of amylose and amylopectin [Vergnes et al., 1998]. The crystallites acting as physical nodes, generate as stress concentrations and thus weaken the material [Van Soest et al., 1996 (b)].

3.4 Thermal stability

The activation energy calculated for the degradation using TGA, for native and thermoplastic wheat flour is $223 \text{ kJ}\cdot\text{mol}^{-1}$ and $90 \text{ kJ}\cdot\text{mol}^{-1}$ respectively [Saiah et al., 2009]. The value of activation energy of native wheat flour is greater than the TPS. This difference is related to the transformation linked to the modifications of crystalline and amorphous phases obtained by extrusion process. The earlier studies on the percentage of crystallinity, using XRD proved that the extrusion causes a reduction in the degree of crystallinity of native wheat flour from 30 to 14% [Saiah et al., 2007]. It indicates that the extruded films have greater amorphous or vitreous phase content. Hence lower amount of energy is enough for its degradation. The effect of lipids (monoglyceride) on thermal stability of TPS is clearly displayed in Figure 10 [Saiah et al., 2009].

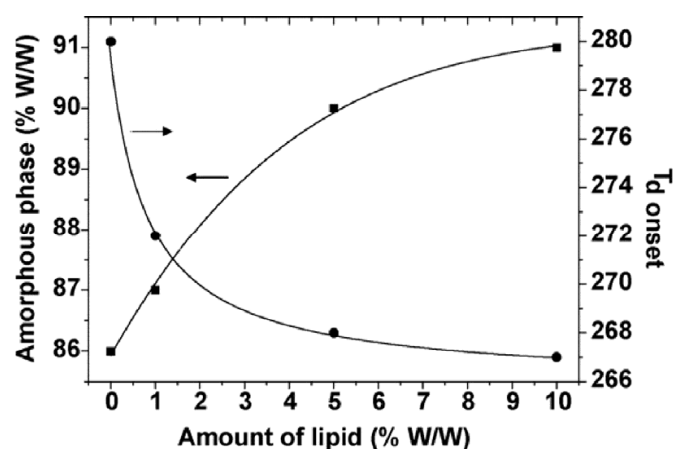


Fig. 10. Variations of amorphous phase content (% w/w) (■) and the $T_{d \text{ onset}}$ (●) of the polymeric material having varying lipid content (0, 1, 5 and 10%, w/w)

It reveals that as the lipid content increases, the $T_{d \text{ onset}}$ value decreases drastically and is more prominent for the materials having lipid content more than 5% (w/w). Here, the monoglyceride has low thermal stability and they start to degrade before the degradation of the matrix. This degradation is more prominent in the matrix having lipid content greater than 5% (w/w). Moreover, the residue at 800°C for all the materials are almost similar ($\approx 12\%$, w/w) since variation in the formulation of the matrix is the amount of the wheat flour and lipid content.

The kinetic aspect of the thermal degradation of polymeric material can be obtained by using Broido method [Broido, 1969]. Here, the assumption is that degradation is a first order or a superposition of first order process and the polymeric material will follow the first order type reactions, i.e. ($n = 1$). The assumption of Broido leads to equation 2:

$$\ln[-\ln(1 - \alpha)] = \ln K - \frac{\Delta E}{RT} \quad (2)$$

where α is the amount of material degraded at time t , ΔE is the change in the activation energy which can also be calculated using the Arrhenius equation, R is the universal gas constant and T is the temperature in Kelvin scale. In this, α can be calculated using the following equation 3:

$$\alpha = \frac{(W_0 - W)}{(W_0 - W_\infty)} \tag{3}$$

where W is the mass at time t , W_0 is the initial mass and W_∞ is the mass after infinite time. The result obtained does not depend upon the value of heating rate and also gives us the activation energy independently of the value of T_m at which the reaction is maximum. Figure 11 represents the Broido plot for the polymeric materials having various lipids content [Saiah et al., 2009].

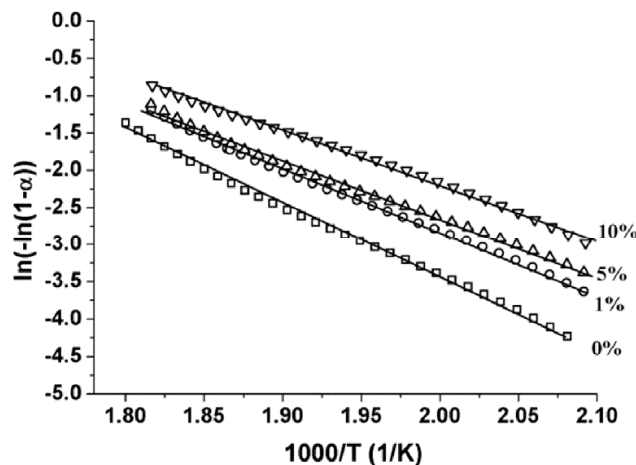


Fig. 11. Broido plot for the polymeric materials having various lipid content (0, 1, 5, and 10%, w/w)

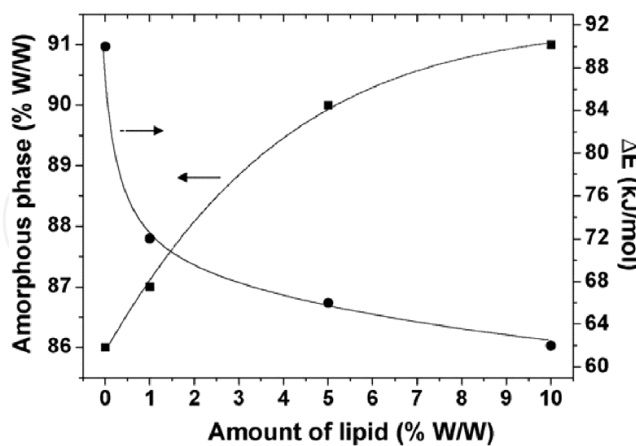


Fig. 12. Variation of amorphous phase content (% w/w) (■) and change in activation energy (●) of the TPS having various lipid content (0, 1, 5 and 10%, w/w).

From this, variation in activation energy were calculated and displayed in Figure 12. When the lipid content increases, the change in activation energy decreases from 90 to 62 kJ.mol⁻¹. This decrease in the thermal stability and change in activation energy is due to the

variation in the degree of crystallinity (Figures 10 and 12) of the polymeric material when the lipids are incorporated.

The influence of the degree of crystallinity on the thermal stability is much clearer by studying the thermal stability of the native and thermoplastic wheat flour. The T_{donset} degradation temperature for native wheat flour is 291°C while that for the thermoplastic wheat flour is 280°C [Leblanc et al., 2008] showing that the thermal stability decreases after the extrusion.

3.5 Glass transition temperature

Figure 13 display the DSC curves obtained for the wheat flour based thermoplastic materials [Saiter et al., 2010].

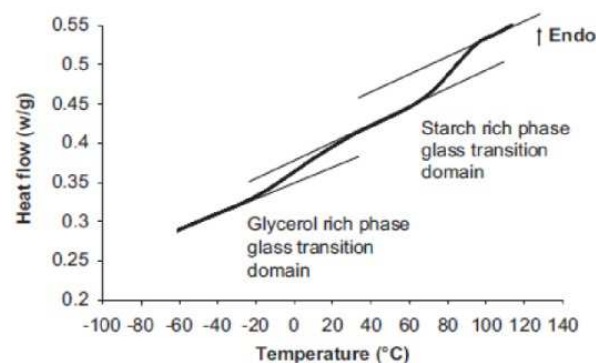


Fig. 13. DSC curves obtained for thermoplastic wheat starch

Only two endothermic steps showing glass transitions are observed at -56 and 10°C, while no peaks for exothermic transitions of crystallization and for degradation. i.e. vitreous and/or the amorphous fraction of the samples are not modified by heat. When the amount of plasticizer changes, the T_g of the starch rich phase is shifted toward the lower temperature. The first transition observed at -56°C is due to the T_g in the glycerol rich phase and the second one at 10°C, due to T_g of the starch rich phase [Saiah et al., 2011].

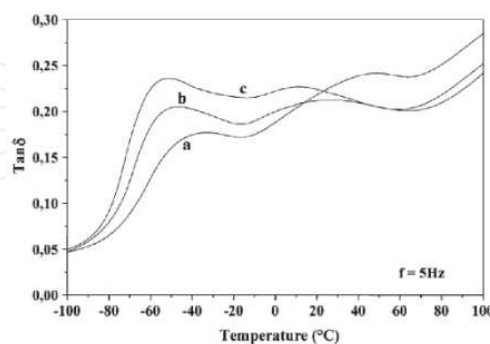


Fig. 14. Dynamic mechanical analysis of wheat-flour based TPS with a: 12,8%; b: 16,5%; c: 20% of glycerol (w/w)

The study of molecular relaxations of TPS having different glycerol content (Figure 14) [Terrie et al., 2010] shows that there are two phases in the TPS: one at lower temperature region corresponding to a glycerol rich phase; another at higher temperature region

corresponding to a starch rich phase. The percentage of glycerol in the matrix modifies the characteristic temperature of these two phases.

Silicon dioxide also affects the molecular relaxations of the matrix (Figure 15), but only the second phase transition of the material i.e. the starch rich phase [Saiah, 2007].

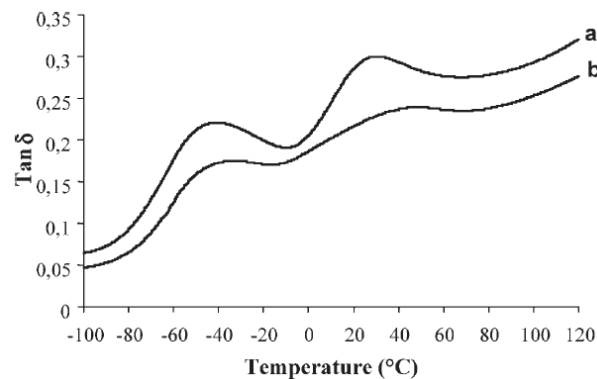


Fig. 15. Dynamic mechanical analysis of wheat-flour based TPS with a: 0%; b: 1%; of silicon dioxide (w/w)

This difference in relaxation is due to the obstacles imparted by silica particles for the starch chain in the starch rich phase.

4. Biodegradation of thermoplastic starch-based materials

Conventional polymeric materials (plastics commonly called) are generally resistant to degradation in the environment due to their high molecular weight and their hydrophobic character. The treatment of plastic waste has therefore become a major environmental concern and programs to recycle, incinerate, or convert waste plastics have been developed. Moreover, the ban on landfill accompanied by concerns related to gaseous emissions from incineration and the difficulty of collection and recycling of certain waste plastics (food packaging, diapers, hospital waste, etc...) stimulated the development of new materials made from biodegradable polymers. These new biodegradable polymers have the advantage of being recycled by composting. However, under industrial composting, the degradation of a product can lead to undesirable compounds and cause a drift of the process. Here the composting process should be carefully validated to avoid disrupting production and protect the environment. Compostability of such materials must first be checked as indicated for instance by the EU directive on packaging (EN 13432), based on the pattern of acceptance below (Figure 16).

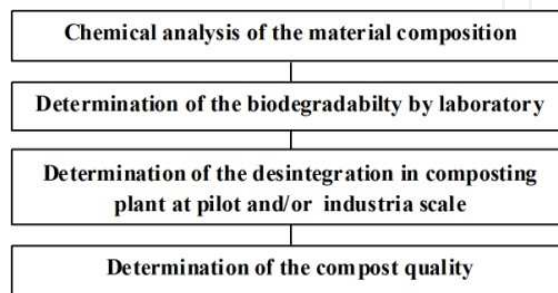


Fig. 16. Scheme of DIN/CEN test used to determine compostability of materials (according to [Pagga et al., 1996]).

In terms of laboratory tests, the standards available about compostability as well ASTM 5338 than ISO/CEN 14 855 measure CO₂ released. But to ensure the compostable property of materials, it is necessary to do carbon balance in solid medium, where:

$$C_t = \boxed{C_g + C_b + C_s} + C_{nd}$$

Cd

Where C_t: amount of carbon material introduced into the degradation medium

C_g: amount of carbon material converted into CO₂ by micro-organisms (mineralization)

C_b: amount of carbon material assimilated by biomass (bio-assimilation)

C_s: amount of carbon material converted into soluble by-product of degradation

C_g + C_b + C_s represent all the carbon degraded (C_d) by micro-organisms.

C_{nd}: fraction of the material which is not degraded or residual material

This approach also allows access to by-products of degradation of the material, which, depending on the material used, can be toxic and persist in the environment.

The materials studied were obtained by extrusion. Once extruded, the films were stored at room temperature (23°C) and controlled humidity (50%). The results presented are those obtained with a co-extruded material, combining PLA and starch. The way of co-extrusion of starch/PLA provides a blend, where the heart of starch (80.6%) is protected on both sides by the PLA (19.4%) which is its outer layer. Thus, the hydrophilic nature of starch is masked by the PLA, which in turn could undergo degradation more important caused of the presence of starch.

4.1 Mineralization in liquid and solid media

The first step was to choose an inert solid medium that simulates the compost and allow the growth of microorganisms, while being devoid of organic matter. The solid inert support used is vermiculite ((Mg,Fe,Al)₃(Al,Si)₄ O₁₀(OH)_{2.4} H₂O): a silicate of aluminum-magnesium-iron that holds water very well. The water activity (aw) is equal to 1 when the water content is adjusted to 70%, so the moisture of the medium was adjusted to this value [Spitzer and Menner, 1996]. Therefore, vermiculite, simulates the structure of aerated compost, allows the proliferation of microorganisms and is completely free of carbon products. The airy structure of the vermiculite also avoids the anaerobic zones and allows simulating, at best, the composting process. The figure 17 illustrates the possibility to use vermiculite to realize composting studies.

Indeed, the difference between the kinetics of mineralization of different media (liquid, vermiculite and compost) is solely due to the moisture content of these environments, humidity higher in the liquid and vermiculite (70%) favoring the degradation of hydrolytic substrate and consequently its availability to the microflora. For cons, whatever the medium, we obtain a final percentage of mineralization is comparable to the order of 74%. Vermiculite can be used to make carbon balance in solid medium [Gattin et al., 2000].

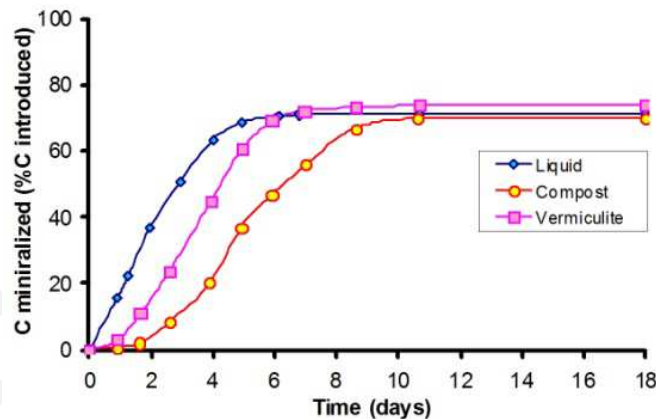


Fig. 17. Mineralization of a ground starch film in liquid and solid media [ASTM D-5209-92 and D-5338-92]

However, it is important to note that the nature of the microorganisms involved in the degradation may be different from one medium to another. Thus, in a liquid medium, the microbial population is predominantly bacterial, while in solid medium, the fungal population is far from negligible. This partly explains the observed mineralization rates since each organism has an efficiency of assimilation of its own. The amount of CO_2 released for the same amount of organic carbon degraded will therefore vary from one organism to another. A faster rate of mineralization induces earlier onset of the plateau phase on the curves of mineralization. Indeed, in this study, the plateau phase of mineralization was obtained from 6 and 8 days in liquid medium, 8 and 9 days in the vermiculite medium and 9 and 10 days in compost. These results are in the same direction as those of Starnecker and Menner [Starnecker and Menner 1996 (a)] who observed the plateau phase after 15 and 40 days respectively in liquid and compost for a starch-based film and those of Van der Zee et al. [Van der Zee et al., 1998] who obtained a plateau phase after 40 and 45 days in liquid and compost in the study of cellulose degradation.

In fact, throughout the study of compostable material, only the final result of mineralization is very important. Therefore, liquid or vermiculite media are relevant approaches to assess the compostability of a material which are readily biodegradable like starch, as the mineralization rate at the end of experiment are the same as those obtained with the compost. These results are consistent with those of Starnecker and Menner [Starnecker and Menner 1996 (b)] and Bellia et al. [Bellia et al., 1999] which showed similar results of mineralization between a compost environment and inert solid medium (vermiculite) inoculated with an extract of the same compost, respectively, for a plastic bag of starch and a thermoplastic material based on polyurethane, polycaprolactone and starch. However, Van der Zee et al. [Van der Zee et al., 1998] found in their study and questioned the relevance of the tests in liquid medium (modified Sturm test) to predict the biodegradation of polymers for biological treatment of waste. These authors have shown that cellulose acetates with a degree of substitution less than 2.5 are easily mineralized into CO_2 in the test compost while no degradation was observed in the test in liquid medium.

Figures 18 and 19 presents the results from mineralization obtained for co-extruded material in each degradation medium according to ASTM and ISO/CEN standards.

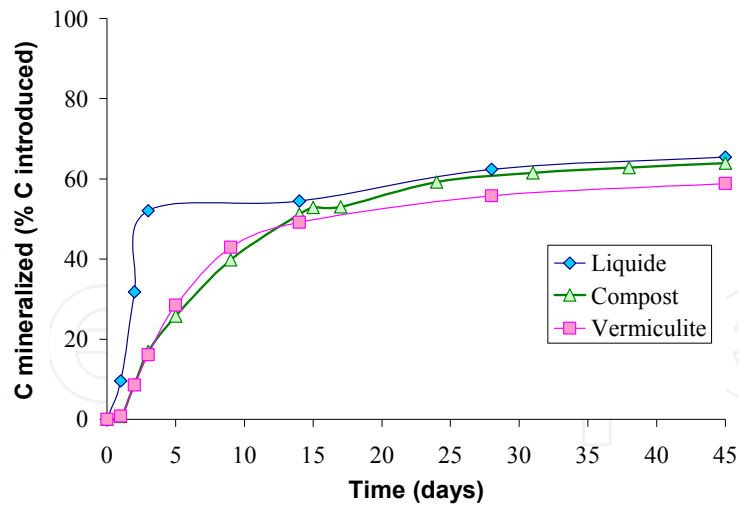


Fig. 18. Mineralization of co-extruded starch/PLA films in liquid (norm ASTM D-5209-92), vermiculite and compost (norm ASTM D-5338-92) media

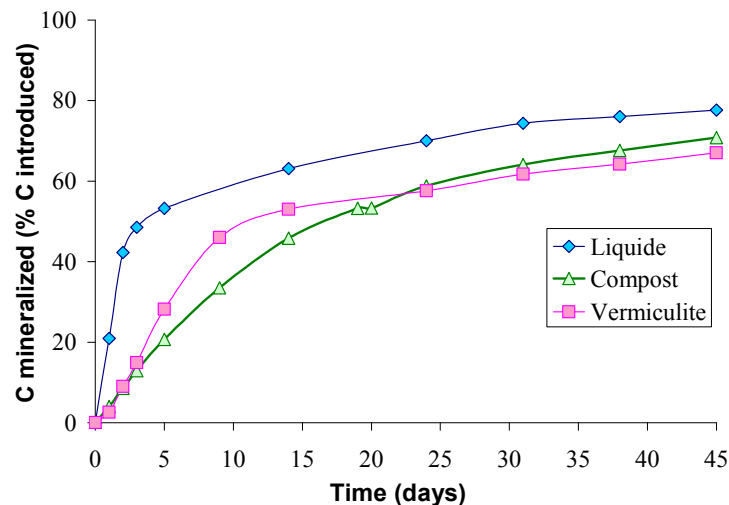


Fig. 19. Mineralization of co-extruded starch/PLA films in liquid (norm ISO/CEN 14852), vermiculite and compost (norm ISO/CEN 14855) media

Whatever the standard used the comparison of degradation in different media shows that the mineralization begins earlier in liquid medium, in agreement with the results for starch alone. In fact, in liquid medium, the mineralization of the co-extruded material is faster than in solid medium and the rate of mineralization obtained after 45 days of incubation is higher than in solid medium for both standards. With ASTM, the difference in mineralization rate between the liquid medium and solid media is small. Indeed, after 45 days of incubation, mineralization rates are 65%, 59% and 63 % for liquid medium, vermiculite and compost. The degradation rate of mineralization of the co-extruded in different environments is as follows: Liquid > compost > vermiculite. With ISO/CEN, this classification is the same, but the differences are much more pronounced since the mineralization rate at 45 days were 78%, 67% and 71% respectively for liquid media, vermiculite and compost.

The degradation of co-extruded starch/PLA was influenced by the standard used to perform the test. This influence comes from the temperature applied during the

degradation. Nature of the environment of degradation also affects the biodegradation of the co-extruded. Indeed, biodegradation of the material was greater in liquid than in other environments, because of hydrolytic degradation. High temperatures coupled with high humidity, are the optimal conditions of abiotic degradation, a prerequisite for biodegradation. However, in solid medium, compost produced results mineralization greater than the vermiculite medium, which was not the case with starch alone. This is probably due to the presence of micro-organisms in the compost which was absent in the vermiculite medium. Indeed, it was shown that the degradation of PLA was predominantly of fungal origin. Fungi, many in the compost, are often more closely attached to the substrate than bacteria. This may explain why in the preparation of the inoculum, the total fungal population was not extracted. Therefore, differences in microbial and fungal compost and vermiculite medium are likely to be different which could explain a higher mineralization in urban compost.

The mineralization rate observed for the co-extruded starch/PLA that were 65, 59 and 63% for liquid media, vermiculite and compost with ASTM and 78, 67 and 71% for the same media with ISO/CEN show that this material is compostable. Therefore, the incorporation of a material which is not readily biodegradable in a biodegradable load promotes biodegradation. This result is consistent with that obtained by Bastioli et al. [Bastioli et al., 1995 (a) and (b)] for a mixture starch/PCL (Mater-Bi class Z) degraded in compost. These authors explain that the degradation of starch increases the surface area of the PCL available to microbial attack. Similarly, Park et al. [Park et al., 1994] showed that the rate of degradation of a mixture injected/molded starch and poly(vinyl alcohol) in the presence of activated sludge (25°C) was similar to that of easily degradable materials like starch alone or cellulose. Chen et al. [Chen et al., 1997] also confirm the positive effect of the incorporation of starch on the biodegradation of poly (vinyl alcohol) in soil at 24°C, the biodegradation of the mixture being more important than that of poly (vinyl alcohol) alone. However, when the polymer coupled with starch is not degradable, Wool et al. [Wool et al., 1990] and Gilmore et al. [Gilmore et al., 1992] showed that the material was only bio-fragmented.

Finally, and regardless of the standard and the degradation medium used, the co-extruded starch/PLA is compostable. All these results thus show that a liquid or solid inert simulates satisfactorily the final result in urban compost. Therefore, if the objective is to conclude positively or not on the compostable property of a material, studies in liquid or vermiculite media, easy to implement, may be sufficient. For cons, the kinetics of mineralization obtained for the co-extruded starch/PLA is different depending on the environment degradation. Therefore, if one is interested in the dynamics of carbon during the degradation of materials, then the use of liquid and vermiculite is not sufficient to simulate what happens in urban compost.

4.2 Application of the carbon balance methodology in solid medium

Carbon balance methodology has been applied to various materials. The carbon balance of co-extruded material has been studied. Figure 20 shows the carbon balance of co-extruded starch/PLLA obtained in the vermiculite medium according to ISO/CEN 14855. Regarding the results of the carbon balances obtained for the co-extruded starch/PLLA, it appears that the choice of the standard on the biodegradation of the material is critical. While 95% of the

carbon ends up in degraded after 45 days with ISO/CEN, the value is less with the ASTM (85%). In addition, moisture of degradation medium favors the rate of degradation of the material. It's interesting to note that the rate of mineralization of this material according to ASTM standard, in vermiculite medium is 59% while the carbon balance indicates that 85% of the material undergoes degradation.

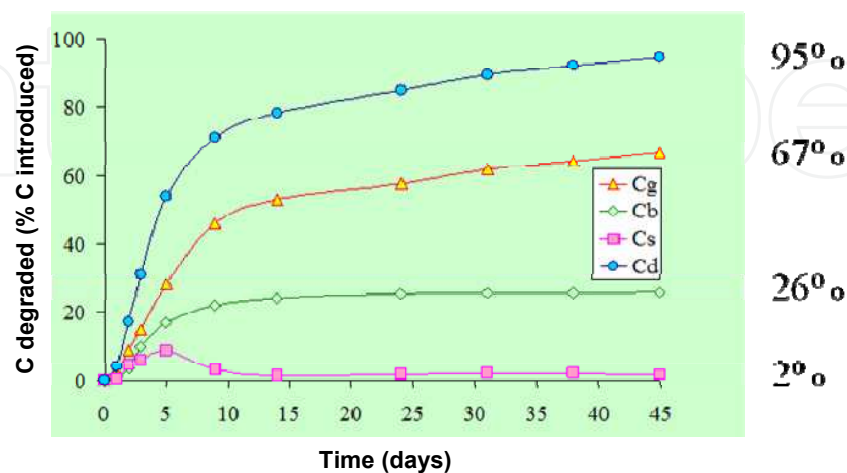


Fig. 20. Carbon balance in vermiculite medium with co-extruded starch/PLLA (ISO/CEN 14855)

In conclusion, the vermiculite medium can be used to make carbon balances and to approach more precisely the degradation process. The recovery rate of carbon was satisfactory regardless of the degradation medium and the substrate studied. At the end of experiment, from 92 to 97% of the carbon has been identified for starch (data not shown), and 100% (liquid medium) for the co-extruded starch/PLA. The study shows that the combination of starch/PLA is an easily compostable material. Moreover, the choice of technology implementation (co-extrusion) allows preparing starch easily accessible due to the grinding before composting process. Considering the results obtained for the biodegradation of co-extruded starch/PLA, this type of complex material is an interesting way to make a compostable material. It remains to optimize the conditions for formatting this type of material so that it can fulfill its function such as packaging and then to verify that the optimized material remains compostable and its degradation by-products as they exist, do not create environmental problems.

4.3 By-products of degradation

The study of by-products of degradation has been proposed for the complex material: co-extruded starch/PLA. In liquid medium, only the presence of glucose, maltose and lactic acid were detected as shown in Figure 21. Initially, only by-products of starch degradation (glucose and maltose) are present. Then, from the 28th day is lactic acid, a byproduct of degradation of PLLA, while we no longer detected by-products associated with the starch. This result suggests that degradation occurs in two stages, first the starch and then the PLA. By cons, for the vermiculite medium, no by-products of degradation have been detected. This would suggest that degradation of by-products is done as they arise.

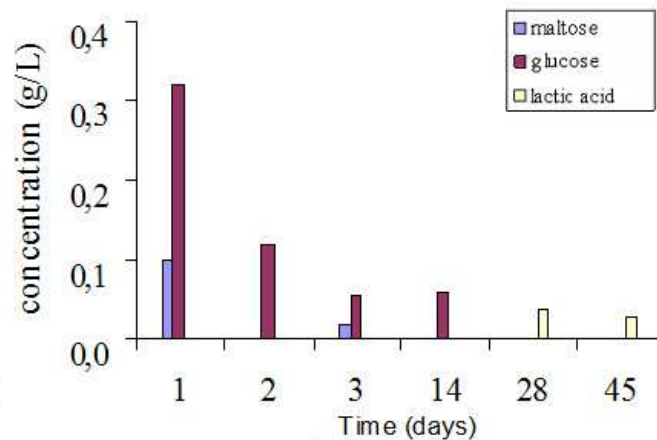


Fig. 21. Evolution of the by-products for co-extruded starch/PLA during degradation in liquid medium using the ASTM standard

4.4 Residual material

Visual observation for starch plates was not possible due to the complete disappearance of the material in the process of biodegradation. Consequently only results obtained with the co-extruded material are presented here (Figure 22).

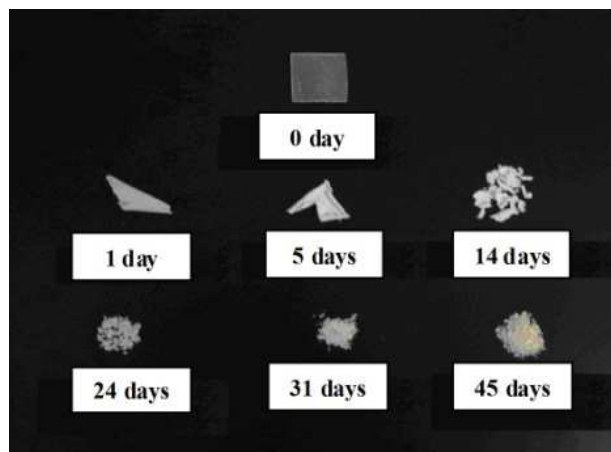


Fig. 22. Physical state of starch /PLA plates during the degradation in liquid medium (ISO/CEN 14852)

The results of our study suggest that the readily biodegradable fraction is degraded first. Indeed, visual observations show that quickly co-extruded material contains only the PLA. This is consistent with the results of Scandola et al. [Scandola et al., 1998], who studied the degradation of Mater-Bi in liquid medium. The compost has showed that after 45 days, the remaining fraction of the material contains only the PCL. In addition, the mineralization rate of the material obtained in this study is 75%, which is similar to our results.

In conclusion, the fraction of non-degraded material can be considered only when its recovery is possible. This shows the important of combining techniques to characterize the material to carbon balances, when the material is with difficulty degraded, particularly to clarify the degradation mechanisms brought into play.

4.5 Mechanisms of biodegradation

The results show that when conditions, especially temperature (ISO/CEN standard) permit it, the two polymers can be degraded together. However, they can also be, as in liquid medium according to ASTM standard, degraded by a fractionated way (Figure 23).

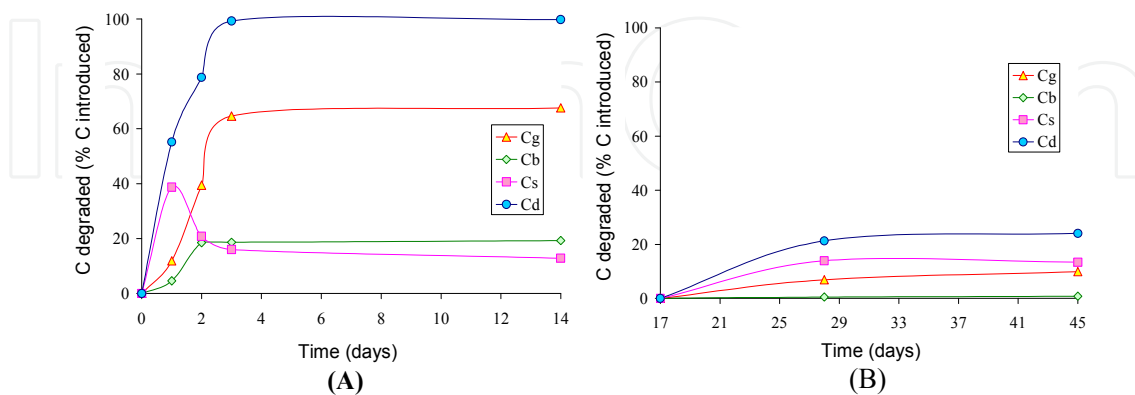


Fig. 23. Carbon balance from starch degraded (A) and PLA degraded (B) during the study of degradation in liquid medium of co-extruded starch/PLA (ASTM D 5209-92 standard)

This behavior is similar to that observed by Mayer et al. [Mayer et al., 1995] who studied the biodegradation in soil and compost of a material combining cellulose acetate from degree of substitution 2.5 and propylene glycol. Indeed, the authors had to extend the incubation to detect weight loss on cellulose acetate in the blend. This fractionated degradation is confirmed by the results obtained for the by-products of degradation (Figure 21). Indeed it appears that the first by-products are related to the degradation of starch, followed by degradation of lactic acid.

This work has also highlighted the influence of starch on the degradation of PLA. Indeed, the percentages of biodegradation were between 82 and 93% for the co-extruded introduced in the form of pieces in liquid and vermiculite media, while the starch is only 80% of the material. Thus, the approach to make compostable materials based on starch by co-extrusion worth pursuing because it would (i) to develop a way to value non-food starch which is a renewable resource abundant and cheap (ii) to limit the fraction of less degradable material by a polymer also derived from renewable resources (PLA), but more expensive than a conventional polymer material (PS, PE, PVC, PET, etc ...) and (iii) to obtain a compostable material for an attractive price.

5. Conclusions

During the last few decades, the studies regarding thermoplastic based on starch have continued due to the severe problems created by the plastic wastages to the surroundings. Up to day, the biodegradable polymers produced are costly and the properties are not competitive with the polymers derived from petroleum. Hence more attention should be given to produce polymers from the agricultural products and from nature. Even though starch can be used for the preparation of thermoplastic, its hydrophilic nature and poor mechanical properties restrict its usage in various applications. Therefore more effective

methods, to increase the properties of the starch thermoplastic by physical or chemical method should be explored. This can result in an increase in the usage of these materials in various applications where life span time and mechanical properties are not too high. Hence the current researches are focused on the modification of starch and also to blend the starch with other thermoplastic polymers to have superior properties. Biodegradation studies indicate that the successful formulation of polymers based on starch can alleviate the problems created by synthetic polymers. Moreover the results from the laboratory scale should be industrialized to have more benefits for the human being as well as to maintain a green environment.

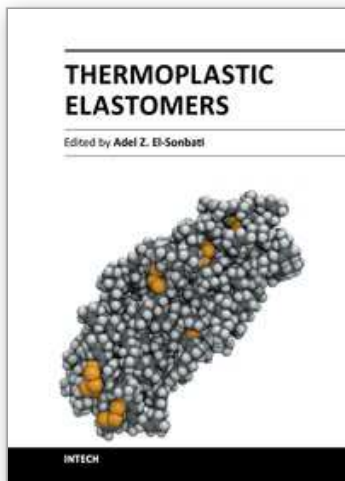
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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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