Research Article

Are 100% Green Composites and Green Thermoplastics the New Materials for the Future?

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A review of the history of the evolution of material science and material technology shows us that one tendency for the future could be the use of agriculture resources. In this work, we review the performances of one of these resources, that is, wheat flour. We show that it is possible to get thermoplastic films with properties quasiequivalent to what is obtained for expensive pure starch. By adding natural fibres, composites are also obtained. These composites exhibit performances which allow their use only for short duration.

1. Introduction

A historical analysis of the evolution and using of materials since the so-called industrial revolution, occurring two centuries ago, shows us that we have to develop new products with the obligation to take into account the end of life and the complete energetic cost associated with their fabrication, use, and afterlife. History tells us that the nineteenth century and the beginning of the twentieth century were the empire of iron and steel or more generally of metallic-based constructions. We have to remember that a train in North America was called iron horse and that the symbol in 1900 of the International Paris Fair was the Eiffel tower. The second important change in materials use occurs after the Second World War which was the use at large scale of plastic materials obtained from petroleum resources. The symbol of these new materials is the nylon used to replace silk in tights.

What will be the future? This is a very difficult question; nevertheless some points can be noted. The first one is linked to the fact that plastic materials have been so largely used that we have too much wastes all over the world. This problem is so drastic today that in many countries the populations want to banish the use of plastic devices like

bags even if these plastic bags are often in polyethylene which is a nontoxic polymer. The second problem is in the real composition of the plastic devices, especially those obtained from thermosetting cured resins. As an example, we may report the composition obtained by means of high-energy X-ray fluorescence performed on an unsaturated polyester resin cured with styrene [1]. More than 12 elements of the periodic table have been found and among them strontium, barium, which may pollute environment even if the amounts are very small (of the order of some PPM).

These plastic materials are obtained from the transformation of petroleum. Even if today the main problem is more the distribution of petroleum rather than the stock, everybody knows that the amount of petroleum available will be smaller and smaller leading to two important consequences. The first is the price, which will increase because of its scarcity, and the price of plastic devices will increase as a result. The second problem will be the cost of transportation which will drastically increase, making it difficult to transport manufactured products.

One of the main consequences is the need to develop new materials coming from renewable resources. These new renewable resources can come from four categories: from classical chemistry, by combining biotechnology and synthesis,

by using microorganisms, and from agroresources. Figure 1 gives a general scheme of these new possibilities.

In this work we will present a review of results of a series of materials obtained from agroresources. The raw material is obtained from wheat flour. As it is of prime importance that the raw material must not be obtained or produced in detriment of the food production, we propose to use a byproduct of the wheat flour production. The materials obtained are thermoplastic films and different composites prepared by incorporating different natural fibres in the thermoplastic films. These materials are made by an extrusion process.

2. Experimental Section

2.1. Raw Materials. The system we have chosen to study is obtained from a formulation based on a wheatflour byproduct, to which different components were added to obtain a film-forming material by an extrusion process. The initial composition of this system is derived from the work previously done at the Laboratory of Engineering Materials (LGMA) of the Engineering School in Agriculture (Esitpa) and has been the subject of a patent [3]. Wheat flour was supplied by the company Grands Moulins de Paris (France). After a division of dry cereal, flour obtained is separated into two categories. The first is rich in protein and will be used by the food industry. The second has low protein content, about 6–7% by mass. In addition to these proteins, it contains 85–88% starch, and the remaining 3–5% consists mainly of lipids and minerals. This second fraction is often reported as a byproduct of wheat flour production and is the subject of this work. In our formulation, wheat flour is incorporated up to 68.2% by mass. The additives used in this work are the following.

- (a) Glycerol provided by the Univar distributor is an agent of both destructive and usually plasticizing properties used in the framework of the transformation and the implementation products containing starch. Its hydroxylated structure confers to this molecule a marked affinity for starch. The glycerol is hygroscopic and has lubricating properties. Its degree of purity is higher than 99%. It is incorporated in height of 12.8% in mass in the formulation of materials.
- (b) Sorbitol provided by the company Roquette, of food quality, is incorporated to a total value of 7.2% in mass in our formulation. Sorbitol is also used as a plasticizer agent.
- (c) Magnesium stearate provided by the company Riedel de Haën, of laboratory grade, is also called octadecanoic acid of magnesium salt. Its molecular formula is $\text{Mg}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$. It contains very little palmitate (ester of palmitic acid). It has the characteristic to break up in the acids and to be insoluble in water. It serves as lubricant. It is incorporated to a total value of 1.8% in mass in the basic formulation.

(d) Silica (Silicon dioxide) obtained by spraying silicon tetrachloride aerosol in a torch burner. Silica prepared in these conditions is not clustered and thus does not require grinding: it is the silica Aerosil 200 with an average diameter of $2\text{ }\mu\text{m}$. It facilitates the passage of the formulation within the extruder. The silica comes from the Cabot Company and is referred under name M5 Cabosil. The rate of incorporation of silica in the formulation is of 1% in mass.

(e) Water is an important constituent which destroys native starch granules and plasticizes the formulation, making the passage of the formulation in the processing machine possible. Water, used is distilled water and it is incorporated in height of 9% in mass in the formulation of our materials.

2.2. Materials Preparation. Raw materials were mixed well before extrusion with the help of a turbo mixer (Kaiser, Germany). This turbo mixer functions with superimposed and shifted blades that turn on an axis located at the center of the tank. The number of revolutions used was 750 rpm, during 5 minutes. This mixer has also a system of dual envelope of cooling with water. Our objective was to obtain the final product as films. Experience showed that it was very difficult to extrude the raw materials to films directly from the mixture obtained from the turbo mixer. This problem was solved by a first extrusion allowing us to obtain granules and then in the second stage using these pellets for a second extrusion to get films with excellent reproducible properties [4]. The pellets were obtained by extrusion with a single-screw extrusion machine (Scamex), at a temperature of 120°C , with a screw speed of 60 rpm and using a granulator. For obtaining films, the second extrusion was carried out with the pellets. The same parameters of temperature and speed were used with a spinneret plate at the exit of the extruder. The principle of the die punt is to distribute the molten matter leaving the extrusion machine to make bands of them. The films obtained have 10 cm of width and 0.4 mm thickness.

2.3. Tensile Experiments. Mechanical tests have been performed with a device consisting in a multipurpose machine of mark “Instron 4301” making it possible to carry out tensile tests, compression, and inflection. The sample, which is in the dumbbell shape, is stretched along its main axis at a constant speed until its rupture. Two properties are recorded: the tensile load (F) applied to the specimen and the displacement (Δl) carried out by the pointer of the extensometer. From these elements, two characteristics of material are deduced.

Tensile stress (report of the tensile load (F) per the unit of area of the initial cross section of the sample (S_0)) is noted as σ , and unit is in MPa

$$\sigma = \frac{F}{S_0}. \quad (1)$$

FIGURE 1: General scheme for the possible new renewable resources for developing new materials [2].

Elongation (or deformation) corresponds to the change in the length per the reference length of the sample (l_0). This strain is noted as ε

$$\varepsilon(\%) = \left(\frac{\Delta l}{l_0} \right) \times 100. \quad (2)$$

For each test, a stress-strain graph expresses the behaviour of material where three principal characteristics are found:

- (i) breaking strength: tensile stress at the instant of the failure of the sample. It is noted σ_{rupture} ;
- (ii) strain at failure: deformation corresponding to the value of tensile stress to the rupture. It is noted $\varepsilon_{\text{rupture}}$;
- (iii) the tensile modulus of elasticity (Young modulus): value of the module provided by the tangent at the origin of stress-strain curve. It is noted E

$$E = \lim_{\varepsilon \rightarrow 0} \frac{\Delta \sigma}{\Delta \varepsilon}. \quad (3)$$

The test parameters are the following: Sensor: 1 kN, Length: $L_0 = 100$ mm, Width: $L = 10$ mm, and sSpeed: $2 \text{ mm} \cdot \text{min}^{-1}$. For our measurements, values of the various mechanical properties obtained for each type of material result from the average carried out on a test specimen of five samples. The uncertainty reported on our results corresponds to the values of the standard deviations obtained.

2.4. Thermogravimetric Analysis. Thermogravimetric studies were performed by thermogravimetric measurements using Netzsch TGA 209 balance (Germany). The measurements

were done on 10–15 mg samples between 20 to 800°C at a heating rate of 10°C/min in nitrogen atmosphere at a rate of $20 \text{ mL} \cdot \text{min}^{-1}$. The calibrations of temperature and mass were made by the manufacturer.

2.5. Dynamical Mechanical Analysis. The dynamic mechanical behaviour of the polymeric material was studied by using TAQ-800 DMA instrument (Thermal Analysis USA). The experiments were performed under tensile mode. The testing temperature ranged from -100°C to 120°C , and the experiments were carried out at frequencies 1, 2, 5, 10, 20, 50, and 100 Hz at a heating rate of $3^\circ\text{C}/\text{min}$. Samples having a dimension of $0.8 \times 20 \times 0.4$ mm were used for the present investigation.

2.6. Scanning Electron Microscopy. Scanning electron microscopy (SEM) (Jeol) was used to analyze the fracture surface morphology. Prior to the SEM imaging, the fracture surface of the sample broken was sputter-coated with about 10 nm thick carbon film.

3. Results and Discussion

3.1. SEM. Figure 2 shows the electron microscope pictures, respectively, of wheat flour before extrusion (Figure 2(a2)) and of the film obtained after the second extrusion (Figure 2(b)). As expected the native granule morphology of wheat flour exhibits a roughness surface topology indicating the presence of impurities, but this image is not drastically different of what is expected for a native wheat starch granule shown also on Figure 2(a1). After the second extrusion the film exhibits the same characteristic of a film obtained from purified starch.

FIGURE 2: Electron microscopy performed on wheat starch (a1), wheat flour (a2), wheat flour-based film obtained after two extrusion process (b), and wheat flour-based film with the two phases (c): the small surface is the plasticizer-rich phase, the other part is the starch-rich phase.

From the same analysis, we have also observed the existence of two phases in the film (see Figure 2(c)). It has been demonstrated that these two phases correspond to one mainly composed of plasticizers (plasticizer-rich phase) while the second is mainly composed of starch (starch-rich phase).

3.2. DMA. The existence of these two phases is well identified by means of dynamic mechanical analysis performed at constant frequency and on a large temperature domain. Figure 3 shows the evolution of $\tan \delta$ with temperature and two transitions, one at $\approx -40^\circ\text{C}$ and a second at $\approx 50^\circ\text{C}$, which are well identified for our standard composition. On the same figure we have also reported the effect of the glycerol content. The temperature of each transition is affected by the composition in glycerol. When the amount of glycerol increases, the temperature of maximum $\tan \delta$ decreases for both transitions. Nevertheless, it is clear that this is the starch-rich phase which is more sensitive to the glycerol content.

3.3. Thermogravimetric Analysis. As mentioned previously, to be able to get a film, we have to add plasticizers, and we know also that these polysaccharide-based materials are very sensitive to water molecules. Thermal stability of our materials was analysed by means of thermogravimetry measurements, and, as shown on Figure 4, it appears that a mass loss occurs for temperature close to 100°C .

We have performed many measurements, and this mass loss is always observed, even if pure starch material is used. This mass loss represents 10% of the initial sample mass. We have demonstrated [5] that this mass loss is the result of water vapour and glycerol evaporation. The second mass loss at a high temperature (300°C) is observed for all polysaccharide materials [6] and corresponds to the destruction of the polymeric chains.

3.4. Tensile Experiments. The mechanical performance has been analysed by means of mechanical testing in stretching mode. Figure 5 shows the results obtained with wheat flour-based films and purified starch-based films. On this figure we have superimposed the results of a series of 5 measurements for each material.

The first comment is linked to the excellent reproducibility of the data in spite of the fact that the raw material comes from natural resources. This good reproducibility is in fact obtained because two extrusions are performed. This leads to homogeneous mixtures, including all the initial impurities in the blends. From these measurements, for the wheat flour-based film we have estimated that the value of the strain at break is close to $\epsilon_{\max} = 16\%$ with a value of stress at break close to $\sigma_{\max} = 3.2\text{ MPa}$. Finally we have estimated a value of modulus at zero strain, $E = 125\text{ MPa}$. These values are not drastically different from what is obtained for a purified starch-based film which gives $\epsilon_{\max} = 30\%$; $\sigma_{\max} = 3.6\text{ MPa}$; $E = 100\text{ MPa}$. The wheat flour-based film

FIGURE 3: Dynamic mechanical analysis performed for three different contents of plasticizer. The glass transition of the plasticizer-rich phase occurs at low temperature $< -40^{\circ}\text{C}$; the glass transition of the starch-rich phase occurs at high temperature $> 20^{\circ}\text{C}$.

FIGURE 4: Thermogravimetric curve obtained on films prepared with purified wheat starch and with wheat flour.

mechanical fragility is directly connected to the existence of defects and impurities.

From the same kind of measurement we can analyse the effect of the plasticizer content (Figure 6(a)) and also the effects of other elements as silica used to have a better extrusion performance (Figure 6(b)).

The effect of plasticizer is found to be drastic on the mechanical performance. Indeed by changing the plasticizers composition from 12.8% Glycerol and 9% water to 21.8% glycerol and 0% water we observed a decrease of 16% for ϵ_{max} , the stress at break σ_{max} decreases by 25%, and the modulus at zero strain E decreases by 35%.

On the other hand, a comparison of the data obtained for films with and without silica (Figure 6(b)) shows that the introduction of silica decreases ϵ_{max} by 21%, but increases the stress at break σ_{max} by 130% while the modulus E is increased by 250%. If the effects of glycerol are well understood, the effects of silica are more difficult to explain. One possible explanation could be linked to the fact that silica is found mainly in the rich phase in glycerol, and its

FIGURE 5: Mechanical test performed on wheat starch- and wheat flour-based films; 5 measurements for each sample are superimposed.

hygroscopic behaviour traps water molecules around it. So by this way silica plays an indirect role of antiplasticizer.

3.5. 100% Green Composites Analysis. When short fibres are added in the formulation before extrusion, a 100% green composite is obtained if the fibre is flax, cotton, sisal, bamboo, and so on. Up to today, flax and cotton fibres have been incorporated in the wheat flour matrix [7, 8]. Figure 7 shows two scanning electron microscope pictures obtained with a wheat flour-based film containing 20% of flax fibres. Figure 7(a) shows that the fibres are homogeneously dispersed in the matrix and oriented in the direction of the film extrusion. Figure 7(b) is a zoom which allows us to have a better analysis of the interface between the fibre and the matrix. Around the fibre, no cavity is observed and when the composite was broken the fibre and the matrix are together broken, no fibre without surrounding matrix or no hole occurring when the fibres is extracted, are observed.

In other words it appears that the interface between the fibre and the matrix is excellent, and we have a good compatibility between the fibre and the matrix. The same results have been obtained with cotton fibres [9, 10].

3.6. Tensile Experiments. When 20% of flax fibres are added, the mechanical performances of the composite are a decrease of 65% for ϵ_{max} , the stress at break σ_{max} increases by 178%, and the modulus for zero strain E increases by 270% to reach a value close to 500 MPa. As an example, the mechanical behaviour obtained with 100% green composites made of wheat flour and cotton is displayed in Figure 8. We observe exactly the same behaviour that was observed previously with flax fibre, but the magnitudes of the variations are smaller. Cotton is less efficient than flax.

From this data we may now compare these 100% green materials to other materials that are produced or used today. Table 1 shows the performances of flax fibres in comparison to inorganic fibres.

If the comparison of flax and glass is done, the flax appears to be the best, but if the comparison is performed

FIGURE 6: Stress-strain average curves for samples with two ratio water/glycerol contents (a) and two silica contents (b).

FIGURE 7: SEM micrographs of a 20% w/w flax fiber composite, at two different magnifications (a) $\times 300$ and (b) $\times 1000$.

FIGURE 8: Stress-strain average curves for samples with various cotton contents (0; 5; 7.5; 10; 15% w/w).

with carbon, this is not the case. So, in many published papers, it is claimed that flax fibres are so good that they could be used instead of glass fibre. But that requires also to analyse carefully the interface of the fibre and the matrix, which is often not so good. This is why flax fibres need to be coated or submitted to a surface treatment. On the other hand two other major problems exist. One is the data dispersion of the flax fibre performances. The second is what happens with the 5 to 10% of water molecules which are very difficult to extract.

TABLE 1: Comparison between flax fibres and inorganic fibres performances.

Nature of fibre	Density	Specific modulus (MNm/kg)
Glass E	2.6	28–30
Carbon	1.7–2	230–600
SiC	2.5	70–80
Flax	1.3–1.5	25–85

TABLE 2: Average values of physical and mechanical performances of synthetic thermoplastic, thermosetting resin and our natural based thermoplastic.

Matrix	Density	Elastic modulus (Stretching) (MPa)
Synthetic thermoplastic	0.9–1.1	1000–2500
Thermosetting resin (polyester)	1.2	3000–5000
Natural based thermoplastic	1.2–1.4	100

For the matrix, we have reported in Table 2 the average values of the mechanical performances of thermoplastic, thermosetting resin, and our natural-based thermoplastic.

TABLE 3: Average physical and mechanical performances of different composites.

Composite	Density	Elastic modulus (Stretching) (MPa)
Synthetic thermoplastic + 30% glass fibres	1.1–1.6	82–220
Moulding high pressure		4000–6000
Thermo setting Resin (polyester) + 30% glass fibres	1.4–2	80–400
Natural based thermoplastic + 20% flax fibres	1.2–1.4	500

It is clear that wheat flour-based matrix does not exhibit the performance required to make a high-technological product. These results show us that such material must be used for short-term applications and will require drastic evolution and amelioration to be used for long-term applications. For these materials, the study of characteristics at the glass transition has been performed, and it was found that these wheat flour-based thermoplastics present a fragility index value [11] comparable to what it expected for a more conventional thermoplastic materials [12].

Table 3 shows the average performances of different composites. The performances of 100% green composites with regard to the mechanical behaviour under strength are not so different from what is obtained for other synthetic-based composites but remains in the order of low-technological applications.

4. Conclusion

As a conclusion, we may say in regards to the data presented in this paper that it is possible to prepare 100% green thermoplastic with raw materials coming from agricultural resources without being in competition with food production. It is also possible to make 100% green composites by using natural fibres or recycled fibres.

Nevertheless, up to today the problem of durability is not well controlled, and the mechanical performance is not good enough to imagine replacing synthetic thermoplastic or thermosetting-based composites.

New investigations have to be done to increase the water protection. This could be done by adding some natural cross-linkers, or by adding a surface protection using natural oils.

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