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Starch-Based Biodegradable Materials Suitable for Thermoforming Packaging*

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In previous works, we had shown that blending plasticised wheat starch (PWS) with biodegradable polyesters improves properties such as the water resistance. The present study was more specifically based on PWS/cellulose fibres composites. In addition, these multiphase systems (blends and composites) have been tested with respect to thermoforming applications. The composites shown an increase in modulus and strength, improved temperature stability and glass transition shifts. After sheet extrusion, each type of materials (blends and composites) was thermoformed. The ageing of the resulting thermoformed trays was tested in storage conditions from 4 °C to ambient temperature, composites based-materials show reduced ageing compared to PWS.

Keywords: Plasticised wheat starch; Packaging; Thermoforming; Cellulose fibres

1 Introduction

Starch has been considered for many years as a polymer with a high potential [1–3] for packaging applications because of low cost, renewability and biodegradability. The feasibility of starch processing using plastic processing equipments has long been demonstrated [4]. During the extrusion of starch, the combination of shear, temperature and plasticisers allows to produce a molten thermoplastic material by disruption of the native crystalline granular structure and plasticisation. This plasticised starch could be suitable for injection moulding or thermoforming. However, only a small number of industrial applications can be presently observed. In fact, different weaknesses limit the utilisation of plasticised starch in packaging applications. Major drawbacks are water sensitivity [5], change of mechanical properties with time [6] (crystallisation due to ageing and plasticisation by water adsorption) and low impact strength resistance. For thermoforming applications, these weaknesses are especially important due to low wall thickness of the produced objects.

In previous publications, we have investigated the behaviour of blends between plasticised wheat starch (PWS) and polyesters [7–9]. Mechanical properties of such materials are in good agreement with classical rules of mixture. Among the different commercial polyesters tested [9], BAK (Bayer, Germany) and Eastar Bio (Eastman, USA) seem to offer a significant degree of compatibility with the starchy phase. For the different polyesters test-

ed, an important decrease in water sensitivity has been measured, whatever the PWS and polyester type and content. Unfortunately, for thermoforming applications, such blends cannot provide sufficient stiffness due to intrinsic softness of the polyesters tested.

Several studies demonstrated the general interest in cellulose fibres used as reinforcement for thermoplastic materials [10–12]. We have investigated the behaviour of PWS/cellulose fibres composites by means of (Dynamic Mechanical Thermoanalysis) (DMTA), tensile and impact strength measurements. Applications of such materials for thermoforming purposes are reported. Packaging storage conditions are also tested.

2 Materials and Methods

Wheat starch was obtained from Chamtor (France). Cellulose fibres (Arbocel) were provided by Rettenmaier (Germany). The characteristics of the fibres are given in Tab. 1. Glycerol was a 99% purity grade according the supplier (Chamtor). This plasticiser was used without further purification.

Tab. 1. Cellulose fibres characteristics (99.5% leafwood cellulose).

Fibre type	Fibre length (<i>L</i>)	Diameter (<i>d</i>)	<i>L/d</i> Ratio
B600	60 μm	20 μm	3
BC200	300 μm	20 μm	15
B400	900 μm	20 μm	45

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Starch/fibres blends were prepared as follows: starch, fibres and glycerol were mixed in a turbo batch-mixer. After dehydration for 45 min in a vented oven at 170 °C, the mixture was stirred and the desired amount of water was slowly added. The resulting “dry blend” was then extruded at 150 °C in a single screw extruder (Scamia, France) equipped with a conical shaped element and granulated. The granules were equilibrated at 65% relative humidity (RH) for 8 days before injection moulding into dumbbell specimen used for mechanical testing. An injection moulding machine (DK Codim 50/100, France) was used with a clamping force of 50 t. The screw barrel was regulated from 100 to 130 °C. Injection pressure was 1500 bar. Holding pressure and time were 1000 bar and 23 s, respectively. Injected parts were moisture equilibrated during several weeks at 50% RH, prior testing.

Mechanical properties were determined at 50% RH and 23 °C. A tensile strength tester (Instron Model 4204, GB) with a crosshead speed of 50 mm/min was used (French standard: NFT 51-034). Impact strength measurements (French standard: NFT 51-035) were performed using the Charpy apparatus (JPS-France) on samples cut out from the central part of injection moulded dumbbells. Thermo-mechanical properties were determined using DMTA (TA Instrument DMA 2980, USA) with a dual cantilever geometry. The measurements were performed at a frequency of 1 Hz and a heating rate of 1.5 °C/min. Samples were coated with silicone wax to prevent water evaporation.

3 Blending PWS and Cellulose Fibres

Several blends were extruded and injected. For all the formulations, the composition of the PWS matrix is the same. The only difference lies in the fibre type and content. The results obtained are presented in Tab. 2. A significant improvement in stiffness is obtained by blending PWS with cellulose fibres that impart reinforcement of the materials. Young's modulus (E modulus) was increased by a factor of 5 to 9 (order of magnitude). For the lowest

fibre content (15%), the modulus increases with the fibre length. The best results are obtained with B400 fibres that have the greatest length, as usually observed for reinforced polyolefins [12]. For higher fibre contents, this phenomenon is not observed, probably due to poorer fibre dispersion. This lower dispersion is mainly observed for the longest fibres.

Similar trends are observed for the maximum strength. Strength improvement depends both on the fibre length and content. Elongation at break decreases with the addition of fibre, this behaviour is also commonly observed with reinforced or filled polyolefins [12].

Thermomechanical behaviour has been studied by DMTA. The evolution of the thermomechanical properties for different materials is presented in Figs. 1 and 2.

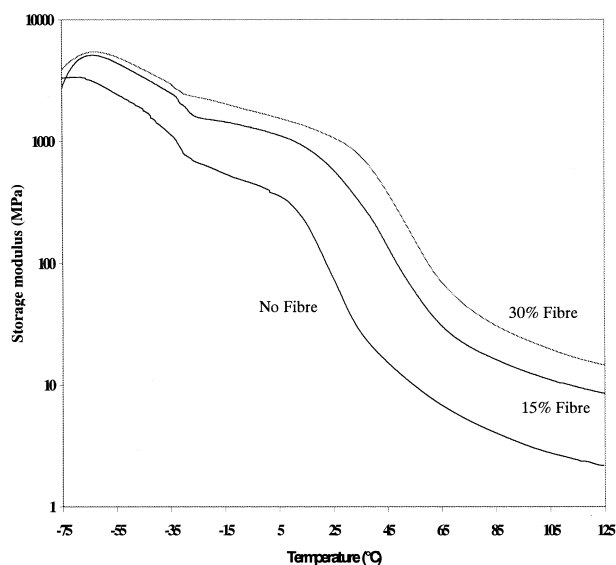


Fig. 1. Thermomechanical behaviour of thermoplastic starch-based materials reinforced with cellulose fibres. Storage modulus evolution versus temperature (fibre contents from 0 to 30%).

Tab. 2. Mechanical properties of PWS-cellulose fibres composites, tensile strength measurements (crosshead speed 50 mm/min, 23 °C, 50% RH).

Type of fibre	Fibre content [% w/w]	E modulus [MPa]	Maximum strength [MPa]	Strain at break [%]
PWS alone	0	52	3	126
B400	15	430	13	31
B400	30	670	22	19
BC200	15	350	10	33
BC200	30	630	15	19
B600	15	296	7	47
B600	30	757	13	10

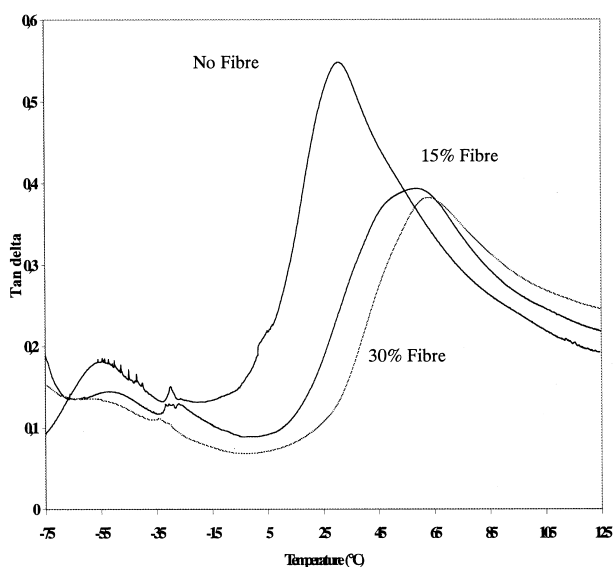


Fig. 2. DMTA analysis of thermoplastic starch reinforced with cellulose fibres, $\tan \delta$ versus temperature (fibre contents from 0 to 30%).

Two main differences are observed between reinforced and pure PWS, i.e.:

- a shift of the rubbery region towards higher modulus for reinforced materials. This shift is dependent on the fibre content and reflects the reinforcing effect of the cellulose fibre. This result has been observed on other systems [10, 11].
- a shift of the glass transition temperature of the matrix towards higher temperatures for reinforced materials (maximum of $\tan \delta$ at 59–64 °C instead of 31 °C for PWS alone). This unusual result could not be explained by a variation of water content, which rather remains constant, but by the creation of strong cellulose-starch interactions that would result in reduced molecular motions of starch chains.

Several attempts were made to tune the properties of reinforced materials and to obtain a stiff material with better

properties, comparable to materials developed in previous studies on PWS/polyester blends. The results are presented in Tab. 3. The plasticised starches referred to as PWS 1 to 3 present increasing glycerol/starch ratios, i.e., 0.14, 0.26 and 0.54, respectively.

When compared with reference materials from pure PWS, the combination with fibres results in a decrease in water sensitivity: mechanical properties are less sensitive at 75% RH storage condition. At 50% RH, almost the same modulus is found for PWS 1 as for the system PWS 3-fibres. From 50 to 75% RH, the modulus of PWS 1 is decreased by a factor of 10 whereas that of the composites PWS 3-fibres is only reduced by a factor of 6. This phenomenon has to be related to the plasticiser content of both formulations. In PWS 1, the glycerol content is low: the material is in the glassy state. In this case, water absorption results in a glass transition shift, providing a rubber-like material at room temperature. On the contrary, PWS 3 is more plasticised and its high mechanical properties are due to fibres reinforcement, but the matrix is on the rubber plateau where it is less sensitive to additional plasticisation by water adsorption.

The plasticiser content is also responsible for differences in behaviour between reinforced PWS 2 and 3. Both materials have similar tensile strength and modulus but very different impact strength resistance. This is explained by the more pronounced plasticisation of PWS 3, resulting in a more ductile matrix. This soft matrix is more likely to absorb the energy during impact, thus resulting in higher impact strength resistance. Obviously, since PWS 3 is more flexible, a higher fibre amount is required to reach the same stiffness as PWS 2 with 20% fibres.

It is therefore possible to tune the properties of the materials according to the specification of various application.

4 Applications to Thermoforming

On the basis of previous results, materials were prepared for thermoforming purposes. The formulations were ad-

Tab. 3. Mechanical properties of PWS-cellulose fibres composites, influence of relative humidity during storage.

Material	% RH	Modulus [MPa]	Impact strength [kJ/m ²]	Strain at break [%]	Max. strength [MPa]
PWS 1 (reference)	50	1110	2	3	25
PWS 1 (reference)	75	100	> 100	60	3
PWS 2 + 20% fibres	50	1150	3	8	26
PWS 2 + 20% fibres	75	n.d.*	n.d.*	n.d.*	n.d.*
PWS 3 + 30% fibres	50	1280	17	6	24
PWS 3 + 30% fibres	75	200	22	15	7

*n.d. = not determined.

Tab. 4. Mechanical results on different systems (PWS+fibres and PWS+polycaprolactone).

Type of material	Modulus [MPa]	Maximum strength [MPa]	Strain at break [%]
A: PWS + fibres	730	14.5	4
B: PWS + CAPA (Solvay)	710	19.5	5

justed to obtain materials with sufficient stiffness (Young's modulus in the range 700–900 MPa). The resulting materials and properties are presented in Tab. 4.

These formulations were extruded to obtain sheets with 0.6–0.7 mm thickness using a plate die (130 °C) and a calendaring system (three rolls at 50 °C). These sheets were thermoformed using a continuous pilot machinery operating in negative mode with blown air. The machine is composed of a heating zone followed by forming in a cooled mould (Autobar Packaging, France). Good forming was achieved with both materials. Thermoforming temperatures were 78 and 90 °C for materials A and B, respectively. These temperatures were lower than those used with conventional polymers, e.g., PVC, PP or PET [13]. The time cycles were comparable to those of the previous conventional polymers. However, the flowing properties of material A are decreased by fibres and small defects appeared on the parts with angles or deep deformations.

To simulate the behaviour of these trays on common conditions, these thermoformed materials were stored in a cold room (4 °C) and at ambient condition for ageing behaviour evaluations. Storage in refrigerator resulted in a marked decrease of material stiffness for both materials that was more pronounced for material A. Storage at room temperature for two months had no significant effect on packaging made with material A, whereas increased brittleness of packaging B was observed after few weeks.

5 Conclusion

Different strategies have been tested in this study to design a starch-based material suitable for thermoforming application. In previous work we have shown that association between PWS and biodegradable polyesters allowed to manufacture materials with improved water resistance. In this study, we have shown that the combination of PWS with cellulose fibres allowed to tune properties of some highly plasticised materials. High stiffness, improved impact resistance and better ageing behaviour was obtained. Both materials (blends and composites) can be processed on industrial-scale thermoforming

equipment to obtain thermoformed trays. We have tested these trays in storage conditions from 4 °C to ambient temperature to simulate a common utilisation of this kind of packaging. In these conditions, the composite materials present a better ageing. To fulfil all the requirements of the packaging industry, a combination of both materials (blend and composite) is being studied in our laboratory that should provide interesting materials presenting improved properties.

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Bibliography

- [1] W. M. Doane, C. L. Swanson, G. F. Fanta: Emerging polymeric materials based on starch, *ACS Symposium Series N° 476*, **1992**, pp. 197–230.
- [2] H. Röper, H. Koch: The role of starch in biodegradable thermoplastic materials. *Starch/Stärke* **1990**, *42*, 123.
- [3] R. L. Shogren: Starch: Properties and Materials Applications, in *Biopolymers from renewable resources* (Ed. D. L. Kaplan), Springer-Verlag, Berlin, **1998**, pp. 30–46.
- [4] I. Tomka: Thermoplastic starch. *Adv. Exp. Med. Biol.* **1991**, *302*, 627.
- [5] H. F. Zobel: Starch crystal transformations and their industrial importance. *Starch/Stärke* **1988**, *40*, 1.
- [6] J. J. G. van Soest: Starch plastics structure-property relationships. Utrecht University (Netherlands). P&L Press, Wageningen, **1996**.
- [7] L. Avérous, N. Fauconnier, L. Moro, C. Fringant: Blends of thermoplastic starch and polyesteramide: Processing and properties. *J. App. Polym. Sci.* **1999**, *76*, 1117.
- [8] L. Avérous, L. Moro, P. Dole, C. Fringant: Properties of thermoplastic blends starch polycaprolactone. *Polymer* **1999**, *41*, 4157.
- [9] L. Avérous, C. Fringant: Association between plasticised starch and polyesters: processing and performances of injected biodegradable systems. *Polym. Eng. Sci.* **2001**, *41*.
- [10] A. Dufresne, M. R. Vignon: Improvement of starch film performances using cellulose microfibrils. *Macromolecules* **1998**, *31*, 2693.
- [11] A. Dufresne, D. Dupeyre, M. R. Vignon: Cellulose microfibrils from potato tuber cells: processing and characterization of starch-cellulose microfibril composites. *J. Appl. Polym. Sci.* **2000**, *76*, 2080.
- [12] A. K. Bledzki, J. Gassan: Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.* **1999**, *24*, 221.
- [13] J. P. Trotignon, J. Verdu, A. Dobracinsky, M. Piperaud: Précis matières plastiques. Nathan, Paris, **1996**, pp. 73–75.

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