Elaboration and Characterization of Starch/ Poly(caprolactone) Blends

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Summary: A starch-based biodegradable material was prepared in two steps. Firstly, starch was chemically modified by using formic acid at 20°C to obtained degrees of substitution of about 1.2. The level of destructuration was also assessed using dynamic rheological measurements. Native starch or starch ester were then mixed with poly(caprolactone) and different polyester oligomers were added as compatibilisers and plasticizing agents. PCL oligomers were found to be the most efficient ones. A significant improvement of the elongation at break of starch formate/PCL/oligo PCL blends was achieved.

Keywords: biodegradable blend; biodegradability; destructuration; O-formylation; PCL; rheology; starch

Introduction

The natural susceptibility of starch to biodegradation has sparked a considerable amount of research to provide starch-containing materials able to undergo rapid biologically induced destruction. Blends of native starch and poly(olefin)s have been largely studied and lead to heterogeneous materials with poor mechanical properties. This low cohesion results from the weak adhesion between starch (hydrophilic) and poly(olefin)s (lipophilic) [1,2]. Moreover, biodegradability of such blends is not complete due the presence poly(olefins). That is why other blends of starch with synthetic biodegradable polymers have been tested. Amongst the available polymers, poly(caprolactone) is one of the most studied. However, the resulting material has also weak properties when using native starch, what can also be improved by the use of compatibilisers or by modification of starch [3-7]. Nevertheless, to achieve this result it is first necessary to, at least partially, remove starch crystalline organization through swelling and gelatinization in water, which can be controlled adjusting the acidic character and the temperature of the medium [8]. Since the 1940's, O-formylation of starch has been widely studied [9-13]. Gottlieb *et al.* [12] have shown that the reaction of formic acid on starch induced the rapid formation of a monoformic ester (DS = 1). According to Wolff *et al.*[10], starch formylation is a reversible reaction where the

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extent of substitution depends on the ratio of formic acid to starch. Recently, Aburto *et al.* [9] have described a route of synthesis of starch fatty acid esters without an organic solvent. At first, native starch is treated with formic acid and then, octanoyl chloride is added to form octanoated starch.

In this paper, we present the destructuration of starch in formic acid and the preparation of starch (formiate) /PCL/oligo polyesters blends and the study of their mechanical and rheological properties.

Experimental

Wheat starch (I59-113H10) was provided by ROQUETTE (France), that is composed of 25% amylose, 75% amylopectin and has a molecular weight of about 50.10^6 $g.mol^{-1}$. Water content was measured by TGA and was found to be 13%. Starch samples were dried at 105 °C for 4h before use to a water content close to 1 %. Formic acid solution 99 % (FA) was used as received from Sigma Aldrich. PCL CAPA 6800 was provided by SOLVAY. Its molecular weight is about 80,000 $g.mol^{-1}$, density of 1.11$g.cm^{-3}$. Polyester prepolymers were provided by DUREZ (table 1).

Table 1. Main characteristics of DUREZ prepolymers.

Oligomer	Nature	Functionnalization	Mw ($g.mol^{-1}$)
P1 : 105-42	1,6- hexane-diol adipate and phthalate	Hydroxyl	2700
P2 : 101-55	Glycol adipate and phthalate	Hydroxyl	2000
P3 : 105-15	1,6-hexane-diol adipate and phthalate	Hydroxyl	7400
P4 : 1063-35	Polycaprolactone	Hydroxyl	2000

50 grams (0.31 mol) of dry native starch were introduced in a three-necked flask containing 250 mL of 99 % formic acid (FA, 6.62 mol). The mixture was stirred at 20°C for 6 hours. Then, the solution was gently poured into methanol (1 L) and filtered off and washed three times with methanol (3 × 300 mL) to remove FA in excess. The samples were then dried in an oven at 50 °C for 24h under vacuum. Degrees of substitution were determined as described elsewhere [14] and measured of about 1.2.

The blends were extruded with a twin screw extruder (Brabender, DSK 42/6) controlled by a Lab-Station with a screw rotation speed of 30 rpm and temperatures of respectively 85,

90 and 95°C from hopper to slot die (4´50 mm^2).

Rheological properties of native starch and starch formate were determined using a THERMOHAAKE Rheostress 1 rheometer with the parallel plates geometry. The samples (native starch or starch formate, 10% (w/w)), were analyzed in dynamic mode with controlled strain. The frequencies range scanned were 0.05 to 50 Hz. All the experiments conducted were isothermal and the temperatures varied from 25°C to 80 °C.

Tensile tests were realized on a MTS Synergie RT1000, using standard ISO527.

Results and discussion

The reaction of starch with formic acid (FA) (Figure 1) was carried out in a thermally isolated calorimeter under mechanical stirring. The stoechiometry between formic acid and starch hydroxyl groups at the beginning of the reaction was 7.05/1.

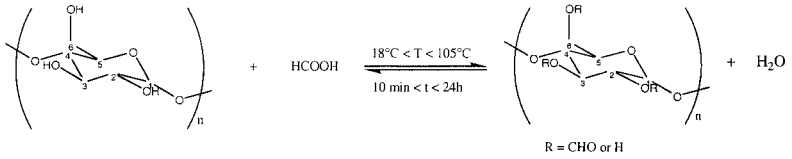

Figure 1. O-formylation reaction on starch.

In order to inhibit depolymerization and color formation, O-formylation was performed on wheat starch at 20 °C for 6 hours and DS measured is about 1.2. Due to their important sensitivity to molecular interactions and structures, rheological measurements were used to characterize starch destructuration during the esterification reaction [15,16]. In excess water, it has been shown that water enters amorphous regions first. Subsequently, it is where the granule swelling occurs. As the temperature increases, crystallites are destroyed, generating both a crystallinity and birefringence loss and leading to the creation of a three dimensional network [17].

In pure formic acid, starch gelatinization proceeds at room temperature (Figure 2). In fact, gelatinization in formic acid occurs at lower temperatures than in water (78°C). Surprisingly, when Tr is increased up to 50 °C, the independent behavior of macromolecules observed at 40 °C disappears and instead, a cooperative behavior is evidenced, indicating a new gel structure. The new gel is a stiffer network than the one at 25-30 °C. This phenomenon may be explained by a competition between chain scissions

due to hydrolysis leading to a higher mobility and an aggregation process of chains resulting from an unknown mechanism but likely due to O-formylation.

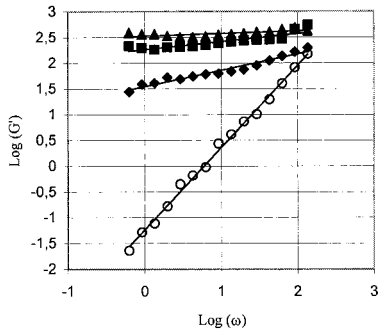

Figure 2. Evolution of the storage modulus (G') with frequency as a function of temperature for native wheat starch suspension in 99% (10% mixture of wheat starch in FA) (gap: 0.3 mm, γ_0 = 8%). ♦ represents G' evolution at T = 25°C, ■ at 30°C, ○ at 40°C and ▲ at 50°C.

Different hydroxyl functionnalized polyester oligomers have been used as compatibilisers of starch/PCL blends. In table 2, we can first notice that starch formate provides blend with PCL with higher modulus than for native starch (Formulations F1 and F2). Therefore, starch acts as a reinforcing agent on PCL which itself exhibit a very low modulus. However, only even for starch formate weak miscibility is expected from the strong reduction of the strain and stress at the rupture. Large starch aggregates are present in the blend and this lack of homogeneous dispersion yields the fragile behaviour observed for the blends. Plasticizing agents have already been claimed by other workers [3-7] and are the aim of the telechelic polyester oligomers that have been studied here.

In comparison with pure PCL/starch blends, the stress at break of PCL/oligomers/starch blends is reduced whereas elongation at break can be enhanced (formulation F1 compared to formulations F3 to F6). The less miscible oligomer (prepolymer P2) yields a material which is very brittle (strain at break 0.4%) without any cohesion. The increase of the molecular weight of the oligomer increases the stress and strain at break in that formulation (F5) which is consistent with the expected behaviour.

PCL oligomer (F6) yields an elongation at break of 191% which is much higher than all the others. This is due to the good miscibility of the PCL oligomer with the PCL but rather strong interaction are also suspected with starch. Moreover, comparing formulations F6

and F7, we can observe that use of formate starch further increase the elongation at break (from 191 to 247%) in comparison to native starch.

Table 2. Melt index flow and mechanical tensile properties of blends containing starch (or formate starch), oligomer and PCL CAPA 6800 40/30/30 (w/w).

Formulations	Starch	Formate starch	P1	P2	P3	P4	PCL	MVI (cm^3/10min)	Module (MPa)	Stress at break (MPa)	Strain at break (%)
Pure PCL							100	8.0	262.0	31.5	693.0
F1	40						60	4.7	655.0	8.9	6.2
F2		40					60	14.0	1095.0	10.1	1.4
F3	40		30				30	18.2	1002.0	2.8	3.6
F4	40			30			30	541.0	828.0	1.7	0.4
F5	40				30		30	22.8	832.0	7.8	11.8
F6	40					30	30	27.1	280.0	5.1	191.0
F7		40				30	30	38.0	266.0	4.0	247.0

This phenomenon, observed only with this oligomer, let us suppose that strong affinity could exist between starch formate and oligomer PCL. In order to verify this hypothesis, different formulations were tested with native or modified starch (DS=1.2). Rheological investigations carried out at 90°C showed that starch formate exhibit a different rheological behaviour in the blends than native starch. The frequency independence of G' and G'' for starch formate blends is the sign of a gel formation which, in turn, is ascribed to a strong destructuration of starch due to strong interactions with PCL oligomer (Figure 3).

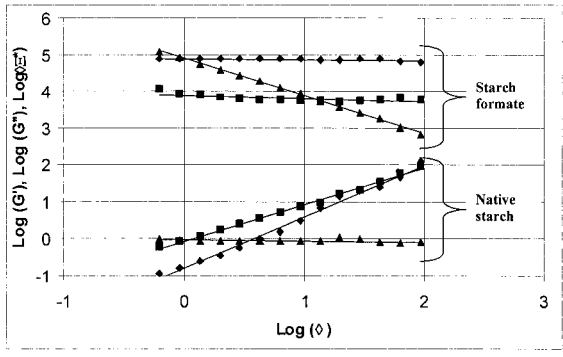

Figure 3. Evolution of the storage and loss moduli (respectively G' and G'') and the complex viscosity as a function of the frequency for native and modified starch mixed with PCL oligomer. (gap: 0.3 mm, g0 = 8%, T = 90°C). ♦ represents G' evolution, ■ G'' evolution and ▲ η* evolution).

Indeed, a gel behavior is deduced from the frequency independent behavior of G' and G'' in the case of starch formate as shown in figure 3. This is not observed for wheat starch/PCL blend which behaves as a dispersion of starch granules in PCL: Destructuration is not sufficient without a high shear at this temperature. This is consistent with the observation made by other groups [5,6]. This rheological observation yields the conclusion of a better affinity of modified starch for PCL than wheat starch. These strong interactions may mostly be due to intermolecular H-bonds oligo PCL/starch formate which substitute amylopectine/amylose interactions.

Conclusion

Storage modulus (G') values measured by dynamic rheometry were found to be sensitive to structural changes of starch as a function of time and temperature of reaction. It was shown that the slope of G' versus frequency (w) was a pertinent parameter to follow both gelatinization and gel destruction and to determine the temperature domain in which the starch has a gel structure in formic acid. Concerning the blends of starch with PCL, it has been shown that O-formylation reaction allows to increase interaction between starch and PCL and that PCL oligomers can act as a platicizing agent to significantly increase the elongation at break of the biodegradable blends.

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