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Biodegradable Compositions by Reactive Processing of Aliphatic Polyester/Polysaccharide Blends

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SUMMARY: Commercially available biodegradable aliphatic polyesters, i.e., high molecular weight poly(ε-caprolactone) (PCL) and polylactide (PLA), were melt blended with a well-known natural and biodegradable polysaccharide: starch either as corn starch granules or as thermoplastic corn starch after plasticization with glycerol. Conventional melt blending yielded compositions with poor mechanical performances as a result of lack of interfacial adhesion between the rather hydrophobic polyester matrix and the highly hydrophilic and moisture sensitive starch phase. Interface compatibilization was achieved via two different strategies depending on the nature of the polyester chains. In case of PLA/starch compositions, PLA chains were grafted with maleic anhydride through a free radical reaction conducted by reactive extrusion. The maleic anhydride-grafted PLA chains (MAG-PLA) allowed for reinforcing the interfacial adhesion with granular starch as attested by TEM of cryofracture surface. As far as PCL/ starch blends were concerned, the compatibilization was achieved via the interfacial localization of amphiphilic graft copolymers formed by grafting of PCL chains onto a polysaccharide backbone such as dextran. The PCL-grafted polysaccharide copolymers were synthesized by controlled ring-opening polymerization of ε-caprolactone proceeding via a coordination-insertion mechanism. These compatibilized PCL/starch compositions displayed much improved mechanical properties as determined by tensile testing as well as a much more rapid biodegradation as measured by composting testing.

Keywords: biodegradable, polyesters

Introduction

During the last two decades, considerable effort has gone into the development of biodegradable polymers, polymer blends and composites. Aliphatic polyesters such as polylactide (PLA) and poly(ε-caprolactone) PCL, represent important biodegradable polymers which are now finding commercial applications as single-use disposable items, in addition to the established applications as medical implants, sutures, and drug-delivery

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systems.[1,2] Both polyesters are actually produced at the industrial scale : PCL by Solvay Interox in UK, Dow Union Carbide in US and Daicel in Japan, whereas PLA is supplied by, e.g., Cargill Dow in US, Mitsui Toatsu and Shimadzu in Japan. While ε-caprolactone is a petrochemical monomer, lactic acid and thus lactide are interestingly produced from non fossil renewable natural resources by fermentation of polysaccharide or sugar, e.g., from corn and beet, therefore allowing the biological cycle to be closed owing to the PLA biodegradation as well as the photosynthesis process.

Combining these synthetic polyesters with natural materials, e.g., polysaccharides such as starch, provides way of cost reduction and combined properties. Unfortunately, simple polyester composites and blends have poor properties because of the lack of interfacial adhesion.[3-5] Indeed it has been reported that the mechanical properties of the aliphatic polyester/starch blends made from various types of starch generally become poorer with increasing starch content. This can be attributed to the incompatibility between the hydrophobic polyester and the hydrophilic starch. Thus, it is expected that the properties of the polyester/starch blends could be improved by proper interface compatibilization.[6-12)]

This paper aims at reviewing two strategic pathways to improve the compatibility within polyester/granular starch blends. Aliphatic polyester/starch compositions have been prepared by mechanical blending of starch (granular or plasticized corn starch with a relative amylose/amylopectine content of 25/75) either with a maleic anhydride-modified polyester, i.e., maleic anhydride-grafted polylactide, or with poly(ε-caprolactone) compatibilized by amphiphilic PCL-grafted polysaccharide copolymers specifically localized at the PCL/starch interface.

Compatibilization of polylactide/starch compositions

In this first procedure, the PLA chains have been functionalized by maleation reaction in order to get reactive functions pending all along the polyester chains, and able to strongly interact with the hydroxyl groups of the polysaccharide phase. The grafting reaction of maleic anhydride (MA) onto the PLA backbone has been performed by reactive extrusion through a free radical process. 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane (Lupersol L101, ElfAtochem) was used as the free radical initiator.[13] Accordingly commercial PLA from Cargill Dow, containing 96% of L-lactic acid units, has been reacted in the molten state with maleic anhydride and in presence of Lupersol L101. Lupersol L101 is FDA approved as food additive and interestingly is characterized by an half life below 1 min at the extrusion temperature range, thus around 180°C. The maleation reaction has been conducted in a co-rotating intermeshing twin-screw extruder with a residence time ranging from 4 to 5 min. at a temperature ranging from 160 to 190°C. The relative content in maleic anhydride has been maintained at 2wt% on PLA basis. PLA being highly moisture sensitive, it was important to check first the effect of the extrusion conditions and more particularly of the extrusion temperature on integrity of the PLA chains. In absence of maleic anhydride and L101, the simple extrusion of PLA triggers a drastic degradation of the polyester chains as evidenced by the decrease of both molecular weight (Mn from ca. 120,000 down to ca. 80,000), solution viscosity, and melt viscosity (Table 1). This degradation occurs whatever the extrusion temperature studied, and more likely results from thermo-hydrolysis and back-biting side-reactions.[14]

Table 1 : Extrusion of PLA chains : effect of the extrusion temperature and L101 relative content on the PLA molecular weight (Mn), polydispersity index (Mw/Mn), intrinsic viscosity [η] and melt flow index under 2.16 kg load at 190°C (MI_2)

Extrusion Temp. (°C)	L101 (wt%)	Mn (GPC)	Mw/Mn	[η] (dL/g)	MI_2 (g/10min.)
-[a]	-	121,600	1.41	1.04	12.76
160	0.00	88,800	1.30	0.82	123.30
160	0.14	124,600	1.81	1.14	4.87
160	0.26	130,400	2.54	1.17	4.08
180	0.00	81,000	1.30	0.83	31.92
180	0.10	104,700	1.33	0.98	13.93
180	0.25	129,000	1.48	1.01	6.99
190	0.00	82,900	1.30	0.79	82.67
190	0.10	114,500	1.33	1.02	19.65
190	0.50	153,600	520[b]	1.72	ND

a) Not extruded sample
b) Highly branched PLA chains (microgel formation)

It is very interesting to point out that the simple addition of L101 to the extruded PLA allows to reduce the lost of molecular weight by free radical self-branching reaction. This is nicely evidenced by the extrusion of PLA conducted at 180°C in the presence of 0.25wt% L101 leading to PLA chains with molecular weight, molecular weight distribution and intrinsic viscosity values very similar to the values measured for the pristine (not extruded) PLA chains. It is however worth noting that at higher temperature and free radical initiator content (Table 1, last entry), highly branched PLA chains (even with microgel formation) are formed as shown by SEC with triple detection which displays a much larger radius of gyration, a large fraction of chains with apparent molecular weight (MW) above 1,000,000 daltons and a Mark-Houwink parameter "a" below 0.5, attesting for the highly branched structure and even the presence of microgels of limited solubility in THF at 25°C.[15] Actually the free radical chain branching of PLA more likely occurs by hydrogen radical abstraction in α position of carbonyl groups, followed by radical addition onto the carbon-carbon double bond of the enolate forms in equilibrium within the polyester chains. At larger extent, cross-linking and microgel formation may take place. Furthermore, free-radical chain scissions might occur and participate in the chain branching process as well.

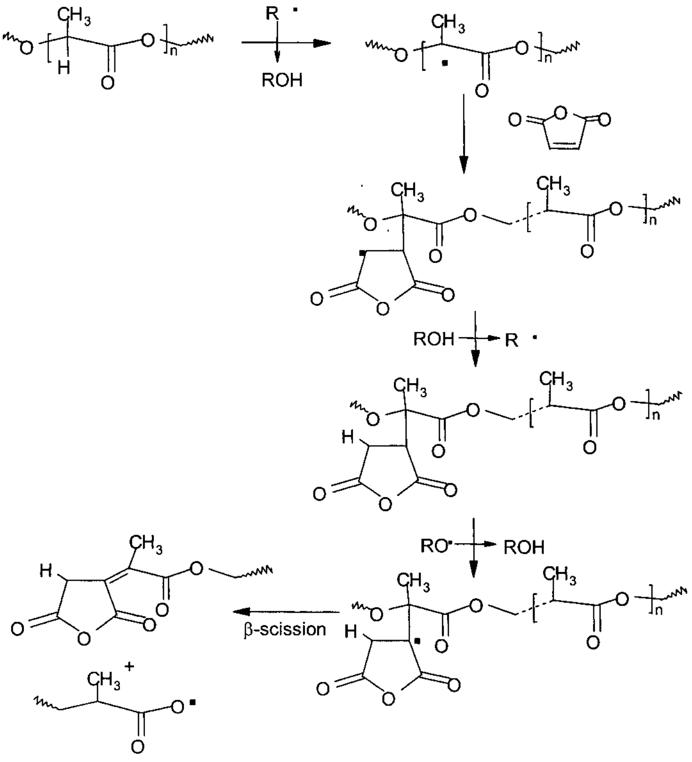
The maleation reaction has been conducted in the presence of 2wt% maleic anhydride at 180°C. Clearly, by increasing the free radical initiator content from 0 to 0.50wt%, the content of maleic anhydride moieties grafted onto PLA chains does increase as checked by back titration of an excess of morpholine with HCl (Table 2).[13] The MW remain quite constant at a value around 85,000, which is more likely explained by a competition between the MW increase through chain branching and MW decrease by β-chain scission triggered by grafted maleic anhydride as shown hereafter (Scheme 1).

Table 2 : Maleation reaction of PLA chains carried out by reactive extrusion in the presence of 2wt% maleic anhydride at 180°C. Effect of L101 relative content on the PLA molecular weight (Mn), polydispersity index (Mw/Mn), and the content of grafted maleic anhydride

L101 (wt %)	Mn (GPC)	Mw/Mn	Maleation (wt %)[a]
0.00[b]	81,000	1.30	-
0.00	81,200	1.25	0.066
0.10	95,300	1.27	0.227
0.25	89,000	1.30	0.475
0.50	85,100	1.31	0.653

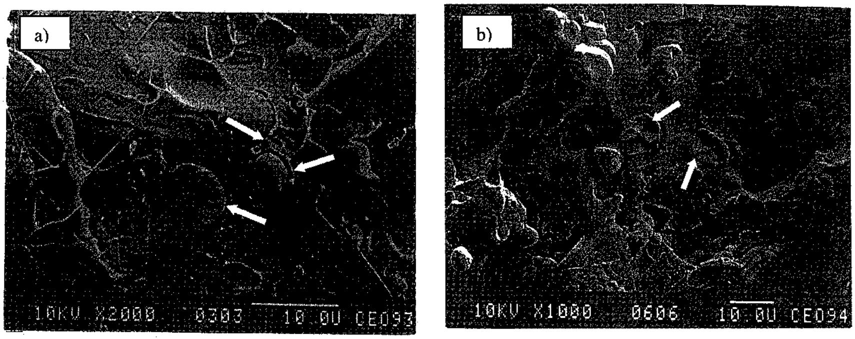
a) Determined by back titration of excess morpholine with HCl
b) No maleic anhydride added to the reaction

Maleic anhydride-grafted PLA (MAG-PLA, here with 0.65wt% maleic anhydride) has been melt blended with granular corn starch in an internal mixer. Cryofracture surface as observed by SEM, displays improved PLA/starch interfacial interactions by using maleic anhydride-grafted polyester chains (Figure 1). Compared to non compatibilized starch/ PLA blends, surface dewetting is no longer observed around the starch particles. This likely results from the strong interactions between carboxylic anhydrides and the hydroxyl functions of the polysaccharide chains. Quantitative characterization of the MAG-PLA/starch compositions by tensile testing but also melt blending with plasticized starch still need to be performed and will be reported elsewhere.



Scheme 1

Figure 1 : Scanning electron microscopy of cryofracture surface of a) corn starch/PLA conventional melt blend and b) corn starch/MAG-PLA (with 0.65wt% maleic anhydride)



Compatibilization of poly(ε-caprolactone)/starch compositions

The second strategy relies upon the PCL grafting reaction onto a polysaccharide backbone. It means that the interface compatibilization has been achieved by using either preformed amphiphilic graft copolymers, actually PCL-grafted dextran (an exo-1,6-glucan polysaccharide) or by generating the graft copolymers via in situ ROP of ε-caprolactone directly initiated from the starch phase.

Thus, in a first series of experiments, PCL-grafted dextran copolymers have been prepared by a 3-step synthesis, involving successively a first partial and reversible protection of the glucosidic hydroxyl functions by silylation (using hexamethyldisilazane as the silylating agent). Then the recovered partially trimethylsilylated polysaccharide chains, now solubilized in organic solvents such as toluene or THF, have been used as multifunctional macroinitiators for the polymerization of ε-CL, the lactone ROP being initiated from the remaining free hydroxyl functions, by activation with either triethylaluminum or tin octoate. The grafting reaction and the ring opening polymerization are both under perfect control and proceed through the so-called coordination-insertion mechanism.[16] The third and last step relies upon the hydrolytic deactivation of the growing species and deprotection of the alcohol groups along the polysaccharide backbone, leading to the expected amphiphilic non ionic PCL-grafted dextran copolymers. This original three-step synthesis as well as the amphiphilic character of the so-obtained graft copolymers have been extensively reported elsewhere.[17] Compatibilization of PCL (CAPA 650 from Solvay Interox with Mn = 50,000)/granular starch blends with 40wt% of granular corn starch has been attempted by adding 5wt% of such amphiphilic graft copolymers. For instance, a copolymer with 60wt% of grafted PCL has been accordingly precipitated onto the starch particles before the melt blending step.[18] One clearly observed improved mechanical properties owing to this interface compatibilization : increase of both material rigidity (Young modulus increases from 265 to 309 MPa), stress at break (from 12.1 to 13.6 MPa) and ultimate strain (from 356 to 417 %). Stress at the limit of elasticity is enhanced as well with an increase from to 8.9 to 10.6 MPa. However, it must be stressed that in addition to the rather time-consuming 3-step synthesis of such amphiphilic copolymers, improved mechanical performances have been obtained only at the condition that the copolymers were first precipitated onto the starch granules assuring their interfacial location upon melt blending PCL with starch at 130°C. This is the reason why it has been decided to directly graft the PCL chains onto starch (either granular or plasticized) by in situ catalyzed ring opening polymerization of ε-caprolactone. Actually, this reaction has been performed in bulk in the presence of $AlEt_3$. Alkyl aluminums are known to be inactive towards the polymerization of lactones but when they react with the OH groups from starch, they yield aluminum alkoxide species able to initiate and further propagate the lactone polymerization.[16] Interestingly, a covalent ester bond is formed directly between the PCL grafts and the starch phase.[19]

First granular starch has been studied and dispersed in liquid ε-CL monomer under vigorous agitation. As a typical example, for an Al content as low as 0.1 wt% relative to the overall 50/50 wt% ε-CL/starch composition, almost quantitative monomer conversion (99 %) could be reached at 90°C within less than 5 min. A grafting efficiency as high as 90 % was determined by tentative selective extraction of non grafted PCL chains in a good solvent such as toluene. By SEM, one can observe that the recovered starch particles are individually and homogeneously embedded/coated within the covalently surface-grafted PCL chains leading to the formation of a "cocoon-like" structure. These surface-grafted PCL chains are long enough to allow crystallization from occurring. A melting temperature at ca. 55°C is measured by DSC. Furthermore, the mean particle size evolution along with the growth of the grafted PCL chains has been checked by laser light diffraction granulometry. Clearly a continuous increase in the mean diameter of the coated starch granules was detected all along the polymerization reaction.[20]

The in situ polymerization of ε-CL and concomitant PCL grafting have proved to be highly efficient with thermoplastic starch, i.e., starch previously plasticized with 25 wt% of glycerol by extrusion.[21] Again fast polymerizations were observed with monomer conversion close to 99 % reached within less than 10 min. and grafting efficiency ranging between 50 and 70 %.

PCL-grafted starch granules have been melt blended with CAPA 650 at 130°C. Typically PCL-grafted starch granules, actually grafted with 24 wt% of in situ polymerized PCL chains, have been investigated (Table 3). At same filler content (i.e., 40 wt%), the PCL covalent bonding allowed for improving both the elastic modulus and yield stress (σ_y) while keeping rather high ultimate properties (stress at break (σ_b) and elongation at break (ε_b)), at least at such high starch relative content. Such a positive mechanical behavior has been attested by markedly enhanced starch/PCL interfacial adhesion as observed by SEM on cryofracture surface. There is no longer surface dewetting/debonding of the PCL matrix all around the hydrophilic starch granules as was initially observed for simple melt blends without any interfacial compatibilization.[21]

Table 3 : tensile properties of PCL (CAPA 650)/granular starch compositions (with 40 wt% starch) melt blended at 130°C. Effect of the covalent PCL grafting onto starch surface (with 24 wt% of grafted PCL relative to starch phase)

PCL/starch (60:40)	σ_b (MPa)	ε_b (%)	Young modulus (MPa)	σ_y (MPa)
PCL/starch	12.1	360	265	9.0
PCL/PCL-grafted starch	14.5	350	320	16.1

Finally, the biodegradability of so-obtained PCL/starch blends has been investigated by composting.[22] For doing so, thin films (ca. 100µm thick) were buried in aerated composting bin for 120 days at 25-30°C (so called natural composting conditions), then followed by 20 days more at a higher temperature of 35-40°C (accelerated final composting). The film weight loss has been recorded along with the composting degradation time. Clearly the film weight loss increases with the starch content, here from 0 to 50 wt% polysaccharide (Table 4). The degradation started first within the starch phase and then occurred within the polyester matrix as observed by SEM.

Table 4 : time dependence weight loss of the PCL/starch films along with the composting degradation time (conditions : see text)

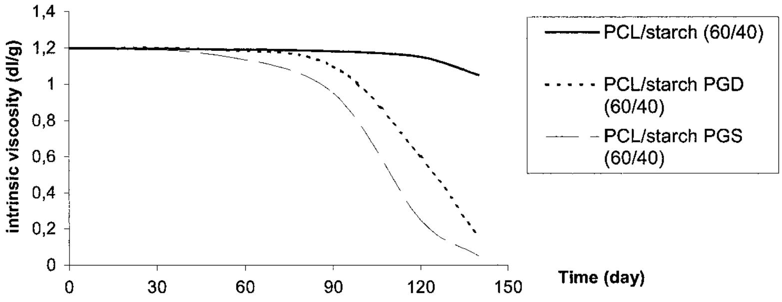
PCL/starch (wt/wt)	Weight loss (%)			
	50 days	90 days	120 days	140 days
100/0	0.45	0.86	1.11	21.18
90/10	1.20	1.63	2.20	40.31
80/20	1.54	1.85	2.30	42.41
70/30	1.73	2.80	3.50	47.21
60/40	6.30	11.10	11.30	53.36
50/50	6.40	11.71	13.36	67.21

It is very interesting to point out the effect of the interfacial compatibilization through either the precipitation of amphiphilic PCL-grafted dextran copolymers onto starch granules (PGD) or PCL-grafted starch (PGS) with only 4 wt% (relative to starch content) of surface-grafted PCL chains which were in situ polymerized as aforementioned. Surprisingly, both compatibilization strategies (PGD and PGS) favor the degradation of the PCL matrix (Table 5). For instance with 40 wt% of starch, the surface of which grafted by 4 wt% of PCL chains, 73 wt% weight loss were recorded after 140 days of composting. This is further evidenced by following the evolution of the PCL intrinsic viscosity along with the composting time (Figure 2). While almost no evolution is observed for the simple starch/PCL melt blend, both PGD and PGS compatibilized samples display a much more significant decrease of the PCL viscosity attesting for a much faster degradation. Such a behavior might find some explanation in the finer and more homogeneous polysaccharide dispersion within the PCL matrix and therefore a larger starch surface contact for the microorganisms.

Table 5 : time dependence weight loss of the PCL/starch films (with 40 wt% starch) along with the composting degradation time. Effect of the interface compatibilization : PGD and PGS (conditions : see text)

PCL/starch (wt/wt)	Weight loss (%)			
	50 days	90 days	120 days	140 days
60/40	6.30	11.10	11.30	53.36
60/40 PGD	4.85	9.06	11.19	67.00
60/40 PGS	12.92	18.96	21.76	73.00

Figure 2 : Evolution of the intrinsic viscosity of the PCL matrix with the composting degradation time



Conclusions

This study has emphasized that biodegradable compositions can be effectively reached by melt blending of granular or thermoplastic corn starch together with commercially available PCL or PLA after adequate compatibilization using reactive melt processing. Accordingly, high polysaccharide relative contents can be targeted leading to improved ultimate mechanical properties and much faster biodegradability as evidenced by composting testing.

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