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Aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization

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Abstract

This paper reports on the synthesis of aliphatic polyester-grafted starch by in situ ring-opening polymerization (ROP) of ϵ-caprolactone in the presence of starch-like polysaccharides that may be granular or plasticized, or a mixture of these, wherein the in situ ROP is conducted in the bulk, i.e. in the absence of solvents. The polymerization is initiated from the starch phase with the amylose/amylopectin hydroxyl functions in the presence of a catalyst such as $Sn(Oct)_2$, or by adequate modification/activation of the surface hydroxyls into titanium or aluminium alkoxides, thereby promoting grafting and good interfacial adhesion between the two starch/polycaprolactone (PCL) phases. Evidence for coupling of the active initiator species onto the starch hydroxyls, aluminium alkoxides for instance, is shown by an aluminium peak in the X-ray photoelectron spectroscopy scan of a starch surface reacted with triethylaluminium. Good interfacial adhesion is confirmed by scanning electron microscopy images of surface fractures and by selective extraction experiments in toluene, which is a good solvent for solubilizing the non-grafted PCL chains. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Aliphatic polyester; Polycaprolactone; Polysaccharide

1. Introduction

During the last two decades, considerable effort has gone into the development of biodegradable polymers, polymer blends and composites using starch [1]. The melt-processing characteristics and mechanical properties of unmodified starch polymers are very poor compared with those of typical synthetic polymers. Some of the problems associated with starch-based compositions include thermal decomposition of starch before melting, water absorption and poor mechanical properties [2,3]. Physical or chemical modification of the starch molecule or granule is a viable alternative to solving some of these problems.

Physical modifications include coating the starch granules with hydrophobic sizing agents similar to those used in the paper industry (such as rosin and silanes), or physically coating the end product with hydrophobic materials like low-molecular-weight waxes and natural resins (zein, rosin, shellac, etc.) and higher-molecular-weight non-polar polymers [4,5]. Crosslinking of the starch granules is another physical modification route to improving the hydrophobicity of starch-like materials. A physico-thermal route to improving the melt processability of starch is by the use of an external plasticizer to solvate the starch granules and enhance the room-temperature flexibility of the final product [6]. In a typical plasticized system with starch, diffusion of the plasticizer out of the product when exposed to low-humidity conditions and diffusion of water into the product under high-humidity conditions are inevitable results. This causes embrittlement of the product due to loss of plasticizer (low humidity) and problems associated with the retention of product shape, texture and form due to excess absorbed water (high humidity). These effects are detrimental especially when water is used as a plasticizer, but are prevalent even in non-water-based starch formulations that incorporate hygroscopic plasticizers such as glycerol, urea, poly(vinyl alcohol) and other related materials.

Chemical modification of starch includes grafting reactions and non-degradative substitution of the hydroxyls on the starch with functional groups like esters, ethers, isocyanates, anhydrides and the like [6–8]. A number of starch derivatives with varying degrees of substitution have been prepared, primarily for food applications and more recently for structural applications. Starch graft copolymers

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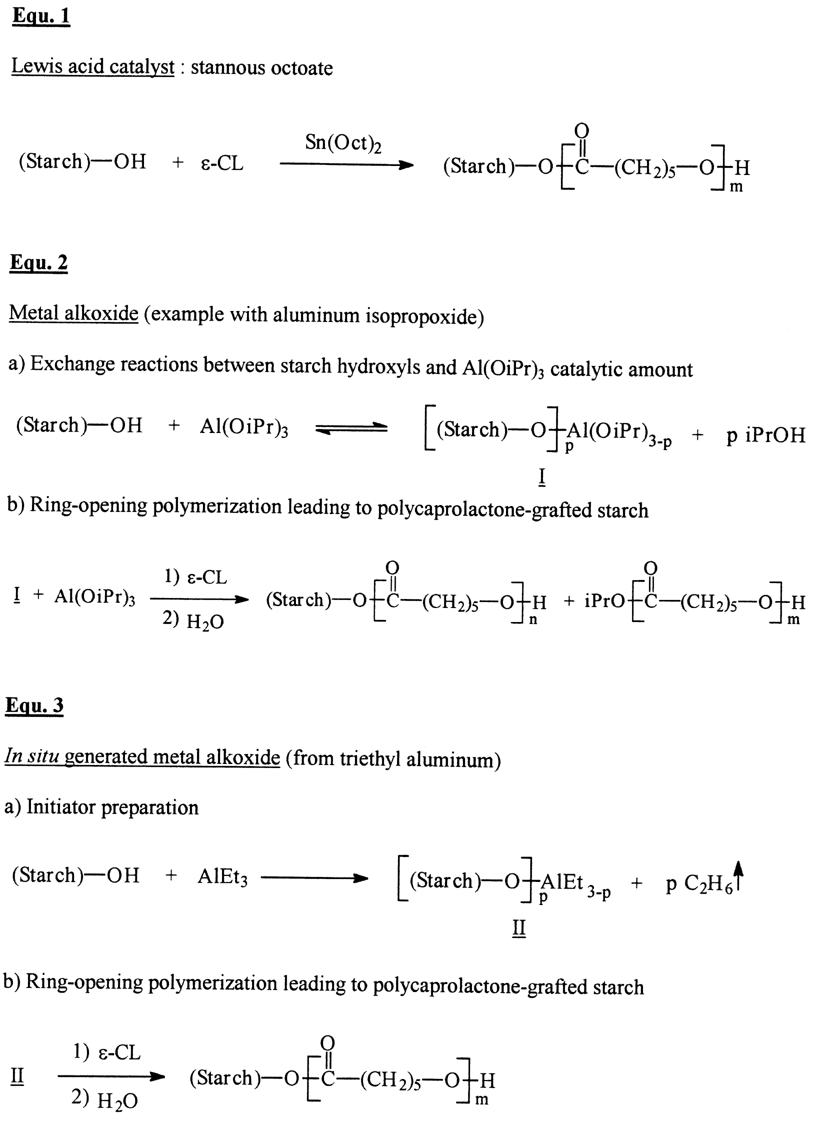
produced from various monomers, including styrene, methyl (meth)acrylate, butyl acrylate, acrylamide and acrylonitrile, containing about 50% starch by weight, have been prepared by a solution process in which the starch grafting was initiated by radiation in the case of styrene and by cerium ions (Ce^{4+}) in the case of other monomers [9–11]. These compositions were extruded directly without addition of plasticizer or homopolymer to give useful products. However, the reaction times for polymerization were of the order of hours. Anionic polymerization of ethylene oxide on starch has also been reported [12]. Reactive extrusion of starch graft copolymers using starch macroradicals generated by shear inside an extruder in the presence of vinylic monomers and/or polymers was studied by Chinnaswamy and Hanna [13].

The focus of this research is on the engineering of biodegradable compositions based on aliphatic polyester-grafted starch-like polysaccharides obtained by mixing starch and a lactone monomer, ϵ-caprolactone, followed by in situ ring-opening polymerization (ROP) of the bulk monomer (without solvents) in the presence of starch, leading to physical and chemical grafting of the polyester chains onto starch. The polymerization is initiated from the starch phase with the amylose/amylopectin hydroxyl functions in the presence of a catalyst such as tin octoate, $Sn(Oct)_2$, or by adequate modification/activation of the surface hydroxyls in aluminium or titanium alkoxides. Use of bulk monomer for the ROP in the presence of starch, fast kinetics enabling the use of an extruder for processing as will be reported elsewhere [14], control over the level of grafting that ranges from 5 to 90 wt%, ease of control of final material properties, and enhanced interfacial adhesion leading to homogeneous encapsulation of the initially moisture-sensitive substrate by a hydrophobic polyester shell, are key advantages afforded by the proposed process. Furthermore, polycaprolactone (PCL) has the rarely met property



Scheme 1.

of being miscible with a variety of polymers, e.g. poly(vinyl chloride), styrene/acrylonitrile, acrylonitrile–butadiene–styrene, bisphenol-A polycarbonate, nitrocellulose and cellulose butyrate, and is also mechanically compatible with polypropylene, polyethylene, natural rubber, poly(vinyl acetate), ethylene/propylene rubber, etc. [15]. Therefore, PCL-grafted polysaccharide-type substrates synthesized by any of the pathways mentioned could be used as compatibilizers in composites of such substrates with various matrix resins, wherein the matrix of the composite is a component that is miscible or mechanically compatible with PCL. It is also worth pointing out that PCL is a biocompatible and biodegradable aliphatic polyester, well known for a valuable set of properties such as non-toxicity for living organisms, resorption after an appropriate period of implantation and good ultimate mechanical properties [16].

2. Experimental

2.1. Materials

ϵ-Caprolactone monomer obtained from Aldrich was stored over 3 Å molecular sieves and purged with nitrogen. Commercial industrial-grade corn starch having a particle size of about 10 μm, plasticized or not, was used and dried either in a forced convection oven at 90–140°C for no longer than 20 h or in a vacuum oven (~0.1 mmHg) at 90°C for 20 h. Catalysts and initiators used were from Aldrich; they were used as received or after appropriate treatment. Tin octoate [stannous 2-ethylhexanoate; $Sn(Oct)_2$] and titanium tetrabutoxide ($Ti(OnBu)_4$) were used as received, without further purification. Triethylaluminium ($AlEt_3$) was obtained in a toluene solution (1.9 M). Freshly sublimated aluminium isopropoxide [$Al(OiPr)_3$] was dissolved in dry toluene obtained by distillation after refluxing over calcium hydride. The concentration of the aluminium alkoxide solutions was measured by complexometric titration of the aluminium atom by EDTA at pH 4.8, after hydrolysis of the aluminium alkoxides by 1.0 M HCl.

2.2. Polymerization procedures

2.2.1. In situ ROP of ϵ-CL catalysed by $Sn(Oct)_2$ [Scheme 1, equation (1)]

In a typical experiment, 15 g of ϵ-CL was added to 15 g of dried, granular or plasticized starch in a 250 cm^{-3} round-bottomed flask equipped with a stirrer and a rubber septum and previously purged with nitrogen. A determined amount of $Sn(Oct)_2$ was then introduced via a conditioned syringe at the desired temperature. Polymerization was stopped by fast cooling to room temperature and monomer conversion determined by selective precipitation of the polymeric fraction and starch in heptane.

2.2.2. Initiation of ROP by aluminium or titanium alkoxides [Scheme 1, equation (2)]

In a typical experiment, 15 g of of ϵ-CL was added to 15 g of dried, granular or plasticized starch in a 250 cm^{-3} round-bottomed flask equipped with a stirrer and a rubber septum and previously purged with nitrogen. A determined amount of initiator—titanium tetrabutoxide, aluminium tri-sec-butoxide or aluminium isopropoxide solution in toluene—was then introduced via a conditioned syringe at the desired temperature. Polymerization was stopped by fast cooling to room temperature and monomer conversion determined by selective precipitation of the polymeric fraction and starch in heptane.

2.2.3. In situ synthesis of aluminium alkoxides by reaction of starch hydroxyl functions and $AlEt_3$ and initiation of the ϵ-CL ROP (Scheme 1, equation (3)]

In a typical experiment, 15 g of ϵ-CL was added to 15 g of dried, granular or plasticized starch (50/50 wt/wt) in a 250 cm^{-3} round-bottomed flask equipped with a stirrer, an oil valve for removal of volatiles and a rubber septum, and previously purged with nitrogen. A determined amount of triethylaluminium in toluene solution was then introduced via a conditioned syringe at room temperature. The reaction medium was then heated to the desired temperature. Polymerization was stopped by fast cooling to room temperature and monomer conversion determined as before. The efficiency of the in situ synthesis of the aluminium alkoxides onto the granular starch was proved by the presence of an aluminium peak in the X-ray photoelectron spectroscopy (XPS; Perkin–Elmer PHI 5400 XPS) scan of the starch surface reacted with $AlEt_3$.

2.3. Determination of polyester grafting efficiency and interfacial adhesion

Selective extraction of the non-grafted PCL chains was performed in toluene at room temperature. Crude product (2 g) was added to 25 ml of dried toluene. After 24 h at room temperature, the insoluble fraction was filtered off, washed with toluene and dried under vacuum (~0.1 mmHg) until constant weight was reached. The insoluble part contains both starch and the polyester chains that were physically and/or chemically grafted on it.

The interfacial adhesion of the starch/PCL composites was checked by scanning electron microscopy (SEM; JEOL JSM-6400) images of the insoluble fraction in toluene and compared with the lack of interfacial adhesion in simple extruded blends of PCL (Tone P-787 from Union Carbide) and granular starch. All samples were mounted on aluminium stubs and coated with gold with a sputter coater.

3. Results and discussion

Polycaprolactone-grafted starch substrates were synthesized from bulk monomer, ϵ-CL, and in the presence of starch by an in situ ring-opening polymerization, resulting in compositions with physical and/or chemical grafting. Three different pathways were used, as represented by the reactions shown in Scheme 1 [equations (1) to (3)]. The reactions were conducted at various temperatures ranging from 60 to 150°C. In the first method, ring-opening polymerization of ϵ-CL was carried out by using a Lewis acid catalyst such as tin octoate in the presence of granular or plasticized starch. Initiation of the ring opening was expected to proceed from the hydroxyl groups from the starch phase [equation (1)]. Indeed, even though the mechanism of ROP catalysed by $Sn(Oct)_2$ is not yet well understood, it is well established that the actual initiation species are hydroxyl-containing compounds, e.g. alcohol or residual water [17–19]. In addition to chemical grafting of the PCL chains onto starch, an improvement of adhesion was also expected by the fact that the polyester chains are growing in close contact to the starch phase.

In the second method, metal alkoxides such as aluminium isopropoxide, $Al(OiPr)_3$, and titanium tetrabutoxide, $Ti(OnBu)_4$, were considered as initiators of the ϵ-CL polymerization. It is expected that exchange reactions between the metal alkoxide groups and hydroxyls from starch or other chemical species added, e.g. hydroxyl-containing plasticizers, generate additional active alkoxide functions [Scheme 1, equation (2a)] that can promote polymerization of ϵ-CL (Scheme 1, equation (2b)]. Very similar rapid exchange reactions between aluminium alkoxides and alcohols were recently observed to occur and allowed to initiate the ROP of ϵ-CL and lactides from both species, i.e. alkoxides and alcohol [20,21]. The so-called 'coordination–insertion' polymerization was under control leading to polyester chains of narrow molecular weight distribution, the mean degree of polymerization of which was determined by the ϵ-CL monomer-to-(alkoxide/alcohol) molar ratio.

The third strategy is based on fixation of the aluminium alkoxide functions onto starch by an in situ reaction between metal alkyls like triethylaluminium and hydroxyl groups of starch. The reaction equilibrium is shifted towards the corresponding alkoxide by the evolution of ethane [Scheme 1, equation (3a)]. According to the previously mentioned ring-opening polymerization mechanism [20,22], grafting of polycaprolactone chains onto starch should be effectively achieved through the covalent ester bridge resulting from the initiation step [Scheme 1, equation (3b)].

3.1. ϵ-CL polymerization catalysed by $Sn(Oct)_2$

The first attempts to prepare starch/PCL compositions (50/50 wt/wt) were performed by in situ ring-opening polymerization of ϵ-CL catalysed by $Sn(Oct)_2$ in the presence of starch at a temperature ranging from 100 to 150°C. The results are summarized in Table 1. Whatever the polymerization conditions, i.e. polymerization of ϵ-CL in solution (10 wt%) or in bulk (without solvent) by starting from granular or plasticized starch (samples 1, 2 and 5), the ϵ-CL monomer conversion is always higher than 98%. However, in the range of tin concentrations studied, very long reaction times, typically of several hours, are required to reach the optimal monomer conversion, in agreement with the thermodynamic monomer equilibrium [17–19]. As could be expected, a temperature increase from 100 to 150°C (samples 3 and 15) results in a substantial decrease of the reaction time (< 3 h).

Chemical grafting of the generated PCL chains onto starch, which was expected from initiation of the ROP by the hydroxyl functions present at the starch surface [Scheme 1, equation (1)], appears to be low as shown by the selective extraction of the crude composite in toluene solution (see Experimental). Actually, 52 to 57 wt% is kept insoluble in toluene after 24 h at room temperature, so that only 4 to 14 wt% of the PCL chains remain attached to the starch surface, more likely through a carboxylic ester linkage as shown schematically in equation (1) of Scheme 1. Such a low grafting level might be explained by a competitive initiation with water contaminating the polymerization medium and by the occurrence of intramolecular transesterification side reactions, the so-called back-biting reactions,

Table 1
Synthesis of starch/polycaprolactone (50/50 wt%) compositions by in situ polymerization of ϵ-caprolactone promoted by $Sn(Oct)_2$

Sample	'Sn' content (wt%)	Temperature (°C)	Reaction time (h)	Monomer conversion (%)[a]	Extraction (wt%)[b]	
					Insoluble	Soluble
1	0.4	100	20	99.5	54	46
2	0.4[c]	100	20	98	53	47
3	0.2	150	5	99	57	43
4	0.2[d]	150	5	98	53	47
5	0.25[e]	150	3	> 99.5	52	48

[a] As determined by selective precipitation of the polymeric fraction in heptane.

[b] As achieved by solubilization in toluene (24 h at room temperature), filtration and drying of each fraction (insoluble = starch + grafted PCL chains; soluble = poly(ϵ-caprolactone) homopolymer).

[c] In toluene (10 wt%).

[d] Tentative swelling of starch in ϵ-caprolactone monomer by agitation at 90°C for 16 h.

[e] Starch plasticized with 25 wt% glycerol in extruder.

leading to the formation of cyclic oligomers [17–19]. Both cases, either ROP initiation by absorbed water or back-biting reactions yield linear or cyclic PCL chains known to be soluble in toluene. Even though the grafting efficiency is low, SEM images of the starch/PCL compositions obtained by ROP catalysed by tin octoate exhibit a much better interfacial adhesion (Fig. 1) compared with simple blends of starch and polylactone (50/50 wt/wt), which are characterized by a total lack of adhesion (Fig. 2). One explanation could be found in the fact that the PCL chains are growing in a close contact to the starch granules, and partially from their surface, resulting in better physical interaction between the two phases. Similar observations have been reported in the so-called polymerization-filling technique in which aluminosilicate particles are surface-treated with a Ziegler–Natta type catalyst before in situ polymerization of ethylene [23,24]. As a rule, polymerization-filled composites (PFCs) have an improved mechanical strength compared with their analogues prepared by melt blending. Although direct evidence is lacking, the superiority of PFCs was attributed to improved wetting of the filler by the growing polymer and to better filler dispersion as a result of the filler surface treatment.

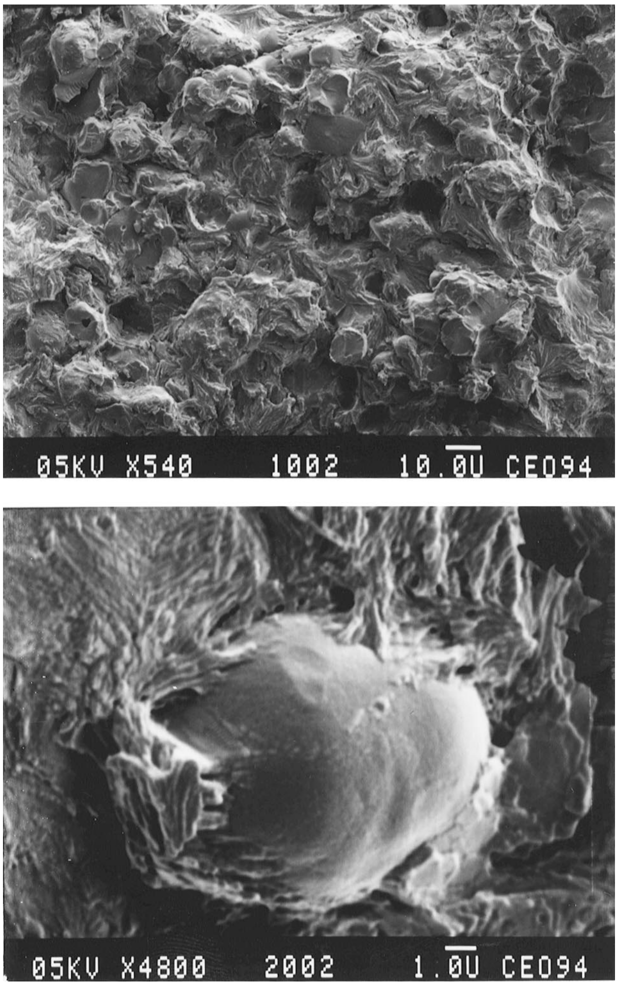


Fig. 1. SEM images of a PCL/granular starch composition (50/50 wt%) prepared by in situ polymerization of ϵ-CL as catalysed by $Sn(Oct)_2$ (see Table 1, sample 3).

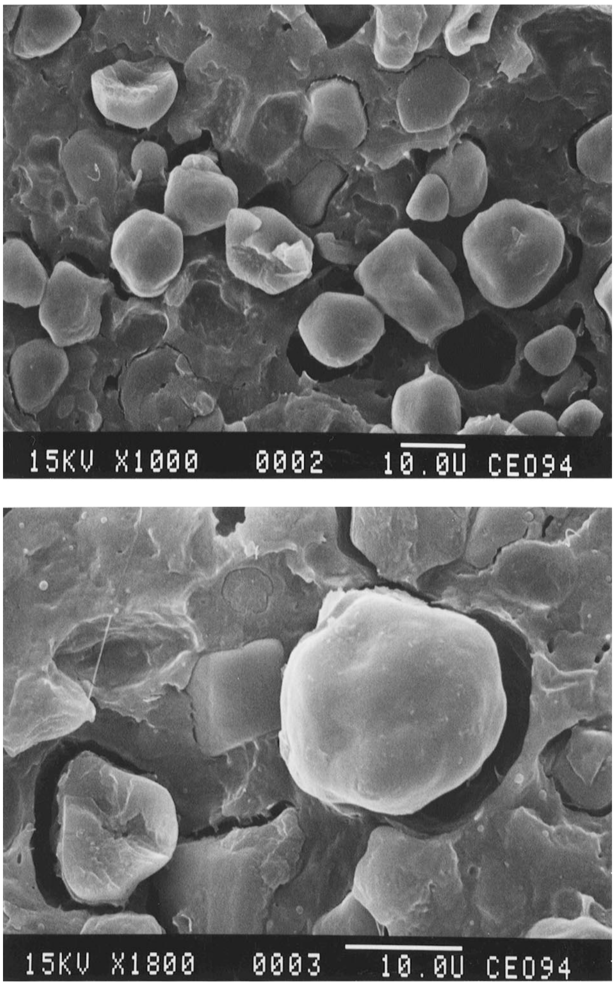


Fig. 2. SEM images of a simple blend of granular starch and PCL (50/50 wt%).

3.2. ϵ-CL polymerization promoted by $Al(OiPr)_3$ or $Ti(OnBu)_4$

The perfectly well controlled ring-opening polymerization of ϵ-CL initiated by $Al(OiPr)_3$ in toluene or tetrahydrofuran (THF) solution has been known for a long time [25]. The polymerization involves a ‘coordination–insertion’ mechanism in which the aluminium atom of the initiator is first coordinated to the carbonyl group of the monomer, followed by its ring opening through a selective ester-bond cleavage. Interestingly enough, $Al(OiPr)_3$ has again proved to be very efficient in promoting homopolymerization of ϵ-CL in the bulk, i.e. in the absence of any solvent (Table 2, samples 1 and 2). In sharp contrast to the very slow kinetics recently reported [21] in bulk polymerization of lactide monomers initiated by $Al(OiPr)_3$, the ROP of ϵ-CL is close to completion within less than 5 min at 100°C. Clearly, such fast kinetics allow the polymerization to be carried out by reactive extrusion so that PCL can be continuously

Table 2
Synthesis of starch/polycaprolactone compositions by bulk polymerization of ϵ-caprolactone, at 100°C, promoted by metal alkoxides such as aluminium isopropoxide and titanium tetrabutoxide

Sample	M(OR)$_w$	'M' content (wt%)	Starch		Reaction time	Monomer conversion (%)[a]	Extraction (wt%)[b]	
			Content (%)	Drying			Insoluble	Soluble
1	Al(OiPr)$_3$	0.05	—	—	5 min	$>$ 99.9	—	—
2		0.15	—	—	3 min	$>$ 99.9	—	—
3		0.025	50	20 h/100°C	18 h	0	50	0
4		0.025	50[c]	6 h/90°C/vacuum	24 h	0	50	0
5		0.15	50	20 h/100°C	20 min	30	52	13
6		0.15	50	20 h/90°C/ vacuum	40 min	18	—	—
7		1.0	50	20 h/90°C/ vacuum	3 h	70	—	—
8	Ti(OnBu)$_4$	1.4	50	20 h/100°C	24 h	98.5	60	40

[a] As determined by selective precipitation of the polymeric fraction in heptane.

[b] As achieved by solubilization in toluene (24 h at room temperature), filtration and drying of each fraction (insoluble = starch + grafted PCL chains if any; soluble = poly(ϵ-caprolactone) homopolymer).

[c] Starch plasticized with 25 wt% glycerol in extruder.

produced under soft conditions. The effect of extrusion parameters, temperature and monomer-to-initiator molar ratio on the ROP kinetics, monomer conversion, extent of transesterification side reactions and molecular parameters of the PCL (number-average molecular weight, molecular weight distribution and melt viscosity) will be the topic of a forthcoming paper [14].

When the polymerization of ϵ-CL is carried out in the presence of granular or plasticized starch that has been previously dried either in a convection oven at 100°C or under vacuum at 90°C, no polymerization occurs so that only liquid ϵ-CL monomer is recovered even after reaction for 1 day (Table 2, samples 3 and 4). The total lack of reactivity might find some explanation in either a detrimental hydrolysis of the aluminium alkoxide functions by residual water or some trapping of the active species in the heterogeneous exchange reaction between the aluminium isopropoxide functions and the starch hydroxyl groups. This exchange reaction being in competition with the ring opening of the monomer, the aluminium content increases from 0.025 to 0.15 wt% when the starch granules are dried at 100°C for 20 h (sample 5). Under these conditions, ϵ-CL can be polymerized effectively but only 30% monomer conversion is reached after 30 min at 100°C. More intensive drying of granular starch (sample 6) or a further increase of the aluminium content up to 1.0 wt% (sample 7) does not improve

Table 3
Synthesis of starch/polycaprolactone (50/50 wt%) compositions by bulk polymerization of ϵ-caprolactone initiated by aluminium alkoxides generated in situ by reaction between AlEt$_3$ and hydroxyl functions of granular or plasticized starch

Sample	Al content (wt%)	Starch		Temperature (°C)	Reaction time	Monomer conversion (%)[a]	Extraction (wt%)[b]	
		Type	Drying				Insoluble	Soluble
1	0.09	Plasticized[c]	6 h/90°C/vacuum	70	5 min	97	82	18
2	0.15		6 h/90°C/vacuum	80	8 min	$>$ 99.9[e]	85	15
3	0.3		6 h/90°C/vacuum	80	6 min	$>$ 99.9[e]	81	19
4	0.3		6 h/90°C/vacuum	110	13 min	$>$ 99.9[e]	81	19
5	0.5		6 h/90°C/vacuum	150	4 min	$>$ 99.9[e]	80	20
6	0.1	Granular	20 h/100°C	80	23 h	0	50	0
7	0.2		20 h/100°C	150	36 min	0	50	0
8	0.3		20 h/100°C	110	7 min	35	—	—
9	0.1		20 h/90°C/vacuum	90	3 min	$>$ 99.9	95	5
10	0.3	Blend[d] (10% G)	20 h/100°C	100	15 min	$>$ 99.9	68	32
11	0.3	Blend[d] (25% G)	20 h/100°C	110	24 min	75	—	—

[a] As determined by selective precipitation of the polymeric fraction in heptane.

[b] As achieved by solubilization in toluene (24 h at room temperature), filtration and drying of each fraction (insoluble = starch + grafted PCL chains if any; soluble = poly(ϵ-caprolactone) homopolymer).

[c] Starch plasticized with 25 wt% glycerol in extruder.

[d] $(100 - X)$ wt% starch and X wt% glycerol (G), with $X = 10$ or 25, blending before ϵ-caprolactone addition.

[e] Foam structure due to evolution of ethane during polymerization process.

the polymerization rate substantially. Even in the presence of a large quantity of $Al(OiPr)_3$, the initially high activity of the aluminium alkoxide functions is reduced markedly by the presence of starch, so as it is reasonable to suspect a trapping of the active species by a strong interaction with the surface hydroxyl groups and a very slow alcohol–alkoxide exchange reaction [21].

Titanium tetrabutoxide has been also checked for its ability to exchange with the hydroxyl groups available at the starch surface and promote the ROP of ϵ-CL (Table 2, sample 8). Even though the polymerization takes place, it requires both a high content of titanium atoms (1.4 wt%) and a long reaction time to reach nearly complete monomer conversion. 20 wt% PCL chains are grafted onto the starch surface as attested by the selective extraction experiment. The partial grafting might be in agreement with the above-mentioned uncompleted hydroxyl–alkoxide exchange reaction resulting in a limited initiation from the starch surface, as proposed in Scheme 1, equations (2a) and (2b). But one cannot completely preclude the occurrence of intramolecular transesterification reactions leading to the formation of cyclic PCL chains that are soluble in toluene. Indeed, titanium tetrabutoxide is known for promoting such back-biting reactions [17].

3.3. ϵ-CL polymerization promoted by aluminium alkoxides generated in situ on starch

First experiments were carried out with starch previously plasticized by 25 wt% glycerol (Table 3, samples 1 to 5). Triethylaluminium in toluene solution was added at room temperature to a plasticized starch suspension in ϵ-CL monomer (starch/ϵ-CL $=$ 50/50 wt/wt) before increasing the temperature rapidly up to 70 to 150°C. A very fast polymerization occurs so that a quantitative monomer yield is reached within a few minutes, i.e. from 4 to 13 min. Although the aluminium content (from 0.09 to 0.5) has no significant effect on the resulting composites, which are characterized by about the same level of polyester grafting (as high as 70 wt%), temperature plays a key role in the composite morphology. At temperature higher than 80°C, ethane evolution resulting from the reaction between triethylaluminium and the hydroxyl groups available from

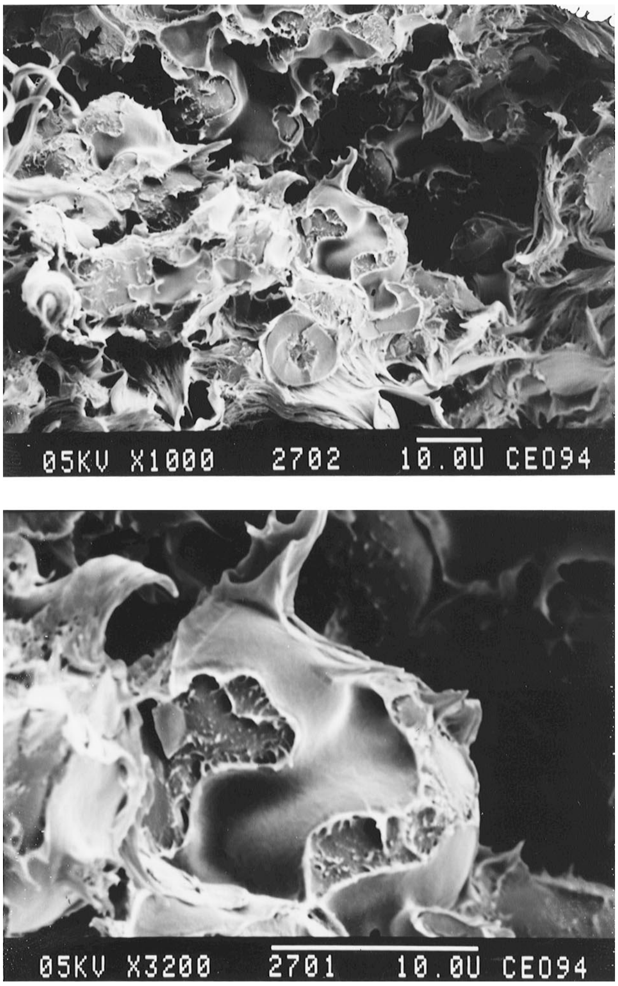


Fig. 3. SEM images of a PCL-grafted granular starch (50/50 wt%) prepared by in situ polymerization of ϵ-CL as initiated by aluminium alkoxide functions fixed at the starch surface (see Table 3, sample 9).

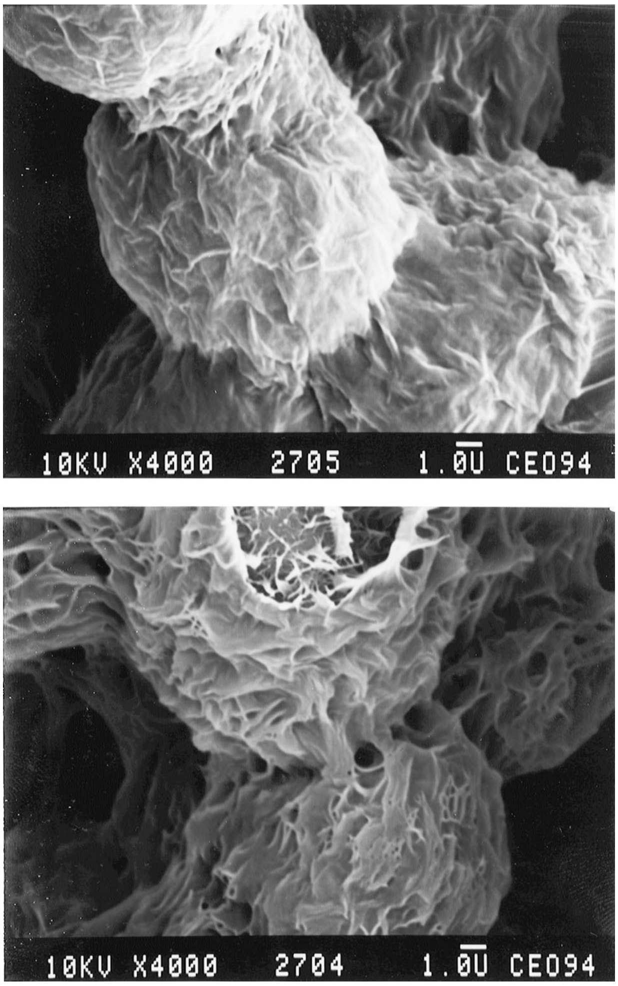
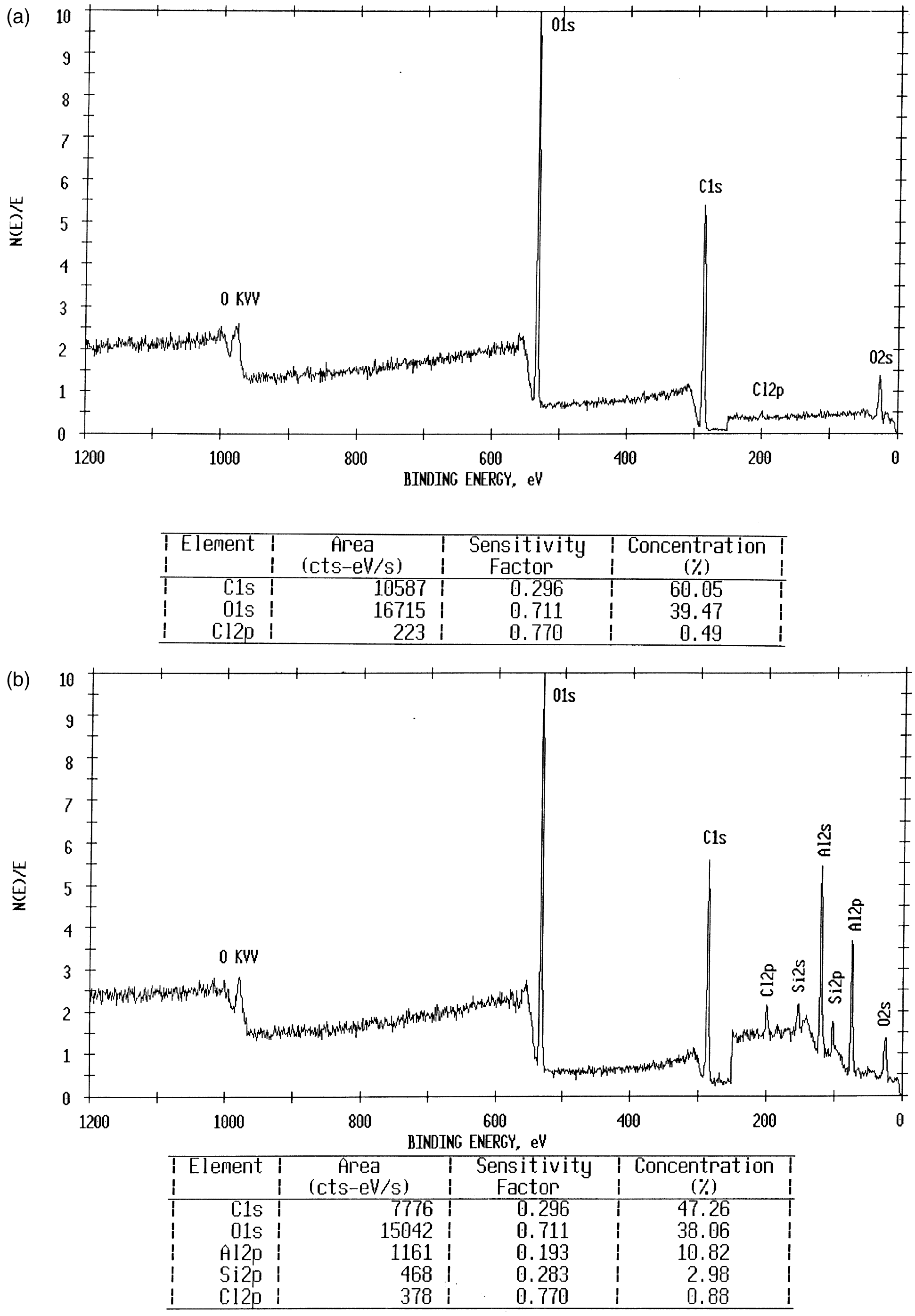


Fig. 4. SEM images of insoluble fraction in toluene of the PCL-grafted granular starch (see Fig. 3).

both the plasticizer and starch, takes place simultaneously with the polymerization. As a consequence, a foam-like structure is formed rapidly, the porosity of which increases with temperature. At 70°C, the polymerization is slow enough to allow the ethane evolution to occur before any increase in viscosity of the reaction medium. Accordingly, a fully dense composite is obtained.

As far as granular starch is concerned, the drying conditions proved to be of prime importance. No or limited polymerization was observed when $AlEt_3$ was reacted with granular starch previously dried at 100°C for 20 h (Table 3, samples 6, 7 and 8). On the contrary, quantitative monomer conversion was reached within less than 3 min when the polymerization was conducted in the presence of starch granules dried under vacuum (10^{-1} mmHg) at 90°C for 20 h (sample 9). Similar to the observations reported previously for the initiation by $Al(OiPr)_3$, residual water should have a strong influence on the ability to generate



Element	Area (cts-eV/s)	Sensitivity Factor	Concentration (%)
C1s	10587	0.296	60.05
O1s	16715	0.711	39.47
Cl2p	223	0.770	0.49

Element	Area (cts-eV/s)	Sensitivity Factor	Concentration (%)
C1s	7776	0.296	47.26
O1s	15042	0.711	38.06
Al2p	1161	0.193	10.82
Si2p	468	0.283	2.98
Cl2p	378	0.770	0.88

Fig. 5. XPS spectrum of granular starch: (a) untreated and (b) after treatment with triethylaluminium in toluene at 85°C.

(or to maintain the activity) of the active aluminium alkoxide species at the substrate surface. In fact, it is well known that alkylaluminium can readily react with water molecules with the concomitant formation of –[Al(Alk)–O–]– aluminoxane derivatives. Even though the ring-opening polymerization of lactones catalysed by methylaluminoxane has been reported [26,27], their activity is much lower than the one determined in ROP promoted by aluminium trialkoxides and dialkylaluminium mono-alkoxides [20].

In addition to the fast kinetics and quantitative monomer conversion (sample 9), a very high level of grafting of PCL chains is determined by the extraction experiment. 90 wt% PCL chains remain attached to the starch granules. It is worth pointing out that the resulting PCL-grafted starch composites show the ability to swell in most of the organic solvents in which PCL is soluble, e.g. toluene, THF, dimethyl formamide, trichloromethane, etc. One can see original applications as inexpensive and totally biodegradable lypogels. In agreement with the high level of grafting, very good interfacial adhesion is observed in SEM images of the crude PCL-grafted starch compositions (Fig. 3). The scanned surface reveals individual starch granules well adhered to stretched PCL threads. From time to time one can distinguish some starch particles broken into two parts and other ones completely coated by a tightly adherent polymeric layer. SEM observations achieved on the insoluble fraction in toluene fully confirm the strong interfacial adhesion since every starch particle is still embedded in a shell of anchored PCL chains (Fig. 4). A key problem has been to determine the molecular weight of the grafted PCL chains since all attempts to either selectively destroy the starch phase or to separate the covalently attached polyester chains, have failed. The only available data come from differential scanning calorimetry (d.s.c.) of the PCL-grafted starch which shows that the molecular weight of the PCL is high enough to allow the polyester chains to crystallize. Actually, the PCL-grafted granular starch (sample 9) is characterized by a melting temperature at 59°C, in agreement with the value commonly met in the literature [22,16].

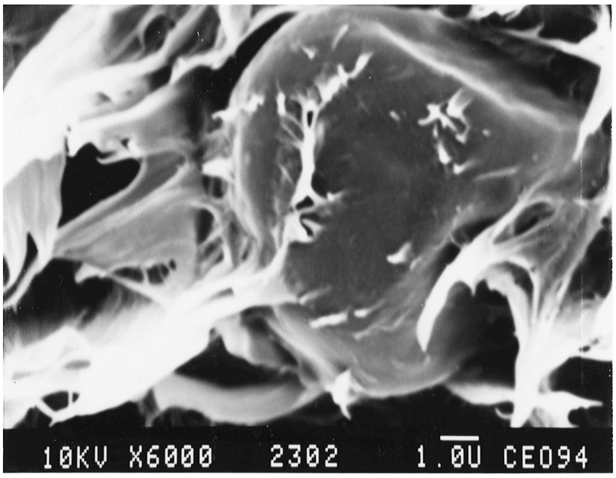


Fig. 6. SEM image of a PCL-grafted granular starch (PCL/starch = 15/85 wt/wt).

Effective fixation of the active initiator onto the starch surface, i.e. the aluminium alkoxides generated in situ by reaction of $AlEt_3$ with the surface hydroxyl functions, was checked by XPS (Fig. 5a and 5b). For this purpose, $AlEt_3$ has been added to a granular starch suspension in toluene (10 wt%) and the temperature increased up to 85°C. After complete ethane evolution and cooling down to room temperature, the surface-treated starch was isolated by filtration, washed three times with dried toluene under nitrogen atmosphere, and then dried overnight under vacuum. In agreement with equation (3a) in Scheme 1, aluminium peaks are detected in the XPS spectrum (Fig. 5b). Furthermore, the recovered surface-treated starch granules were reacted with ϵ-CL (without any solvent) at 100°C for 2 min. The crude PCL-grafted starch (15/85 wt/wt) was examined by SEM, which shows starch particles attached to stretched polyester threads (Fig. 6). Similar results have been obtained from starch granules pre-blended with 10 or 25 wt% glycerol, before the ϵ-CL polymerization at 100 and 110°C, respectively (Table 3, samples 10 and 11). However, longer reaction times were required for finally reaching lower grafting efficiency.

4. Conclusion

Polycaprolactone-grafted starch has been synthesized by in situ ring-opening polymerization (ROP) of ϵ-caprolactone in the presence of granular or plasticized starch. Polymerization was carried out in the bulk (without solvent) and was initiated from the starch hydroxyl functions in the presence of a catalyst such as $Sn(Oct)_2$, or by adequate modification/activation of the surface hydroxyls into titanium or aluminium alkoxides. The latter species, i.e. aluminium alkoxides generated in situ by reaction of triethylaluminium with the starch hydroxyl functions, proved to be the most effective in promoting fast polymerization and also covalent grafting of the polyester chains onto the starch phase. The grafting efficiency can be as high as 90 wt%. It results in very good interfacial adhesion as attested by SEM observations achieved on samples before and after a selective extraction experiment in toluene. Owing to the fast kinetics and the rather soft polymerization conditions, reactive extrusion in a twin-screw extruder has been conducted. These results, as well as the physico-mechanical properties of the extruded composites, will be reported in the near future [14].

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