Grafting Biodegradable Polyesters onto Cellulose

Xavier Samain, Valérie Langlois, Estelle Renard, Gérard Lorang

Institut de Chimie et des Matériaux Paris-Est UMR 7182, Université Paris Est—CNRS, Systèmes Polymères Complexes, 2 à 8 rue Henri Dunant, 94 320 Thiais, France

Received 2 July 2010; accepted 23 October 2010
DOI 10.1002/app.33659
Published online 28 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: To increase the compatibility between cellulose fibers and polyester matrix an original method for grafting hydrophobic oligoesters onto cellulose was proposed. Two kinds of cellulose substrates were employed as cellulose films and microcrystalline cellulose powder. Different oligoesters containing reactive end groups based on poly(DL-lactic acid) PDL-LA, poly(ε-caprolactone) PCL and poly(3-hydroxyalkanoate)s PHA were first prepared and characterized by size exclusion chromatography (SEC), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC). The carboxylic end groups of the polyesters were activated using thionyl chloride ($SOCl_2$) to increase the esterification reaction with the hydroxyl groups of the cellulose. The esterification was realized in a heterogenous medium without any catalyst by deposition of chloride oligoesters in solution (2–100 g L^{-1}) onto cellulose film at different temperatures (25–105°C) during 1–12 h. The successful grafting on the various substrates was confirmed on the basis of FTIR spectroscopy, contact angle measurement, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). In particular, it is shown that a small quantity of grafted oligoesters led to a significant increase of the hydrophobic character of the cellulose with a contact angle near 130°. The increase of hydrophobicity of cellulose is independent of the nature and length of grafting oligoesters. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1183–1192, 2011

Key words: poly(3-hydroxyalkanoate); cellulose grafting; surface modification; biodegradable polyesters

INTRODUCTION

Growing environmental consciousness and changes in public legislations have led to the important demand for environmental friendly materials, especially for bio-composites produced from the combination of natural fibers and synthetic or biodegradable/bio-based polymers.[1] The advantages of natural fibers are low cost, low density, sustainability, and recyclability as well as competitive specific mechanical properties.[2] Among the biodegradable polyesters, we can distinguish petroleum-based polymers as PCL and renewable resource-based polymers as PLA and PHA. Various research groups have studied the suitability of these polymers[3–12] to be used as matrix in composites. The major disadvantage of the materials containing cellulose fibers and polyesters is the low-grade fiber–matrix adhesion due to the difference in the surface properties of both components. Indeed, the intrinsic hydrophilicity of cellulose containing many hydroxyl groups contrasts with the polymer hydrophobicity. The stress transfer at the interface between two different phases is determined by the degree of adhesion. In the considered case, the interface between natural fibers and the polymer matrix represents the weakest property of these materials. Coupling agents are known to facilitate the optimum stress transfer at the interface.[13–15] To improve interfacial adhesion between fibers and PHB, different methods have been studied based on the increase of hydrogen bonding using dihydric phenols,[6] using silane coupling agent on flax fibers,[16] esterification of fibers,[17] or addition of plasticizers.[18] Graft copolymerization of maleic anhydride has allowed the preparation of PHB bearing pendant anhydride groups[19,20] with enhanced adhesive strength toward natural fibers. Another method consisted in the modification of the cellulose substrate using the "grafting from" approach where synthesis of the polymers is based on the formation of radicals by various chemical initiators or atom transfer radical polymerization.[21] Recently, Lönnberg et al.[22] has developed the ring opening polymerization (ROP) of ε-caprolactone and L-lactide from cellulose surface for the covalent bonding of the respective polymers on fiber samples.

A new "grafting onto" method to improve the fiber–matrix adhesion between cellulose and biodegradable polyesters has been developed here in easy experimental conditions. The method is based on the grafting of oligoesters onto cellulose surface. Oligoesters as PHB, poly(3-hydroxybutyrate-*co*-hydroxyvalerate) PHBHV, poly(3-hydroxyoctanoate-*co*-3-hydroxyhexanoate PHO, PCL and P(DL-LA)

Correspondence to: V. Langlois (langlois@icmpe.cnrs.fr).

© 2011 Wiley Periodicals, Inc.

were used for grafting onto cellulose films and onto microcrystalline cellulose powder. The oligoesters containing a carboxylic end group were reacted with thionyl chloride to obtain chloride oligoesters. Direct grafting by esterification was realized by deposition of a solution of oligoesters onto cellulose. Different parameters as the reaction temperature, the concentration of the solution and the time of reactions were tested in a view to determine the best experimental conditions. Different oligoesters were grafted to study the influence of the nature and also the length of the oligoesters on the hydrophobicity properties of the cellulose. The grafted substrates were characterized with the FTIR, XPS, contact angle measurements, and TGA to study the modification of hydrophobicity of the cellulose after grafting.

EXPERIMENTAL

Materials

PHB was kindly supplied by Biomer (Munich, Germany), poly(3-hydroxyoctanoate-*co*-3-hydroxyhexanoate) noted PHO, was prepared using Pseudomonas sp Gpo1 (CNRS, Cermav, Grenoble, France) with an average molar mass of 80,000 ($I_p = 2$) as described in a previous report.[23] PHBHV containing 12% of 3-hydroxyvalerate was supplied by ICI. ε-CL, hexanoic acid and thionyl chloride were purchased from Aldrich and used as received. Microcrystalline cellulose powder was purchased from Sigma.

Oligomers of P(DL-LA) were supplied by Galactic. Wood fibers were supplied by Ahlstrom, Pont-Eveque, France, in form of paper rolls (323, 123, and 109 μm in thickness) containing 28% of soft wood and 71% of hard wood.

Preparation of PHA oligomers

Oligomers of PHB, PHBHV and PHO were obtained by thermal treatment. PHA was introduced in a three-necked 25-mL flask with argon current and mechanical stirring. The flask was maintained under magnetic stirring at different temperatures depending on the nature of PHA, and for a predetermined time to obtain the desired molar mass. The reaction was stopped by an ice bath. Oligomers were purified by dissolution in CH_2Cl_2, precipitation in ethanol, filtration, and vacuum-drying for 24 h.

Preparation of PCL oligomers

Oligomers of PCL were obtained by ring opening-polymerization of 5 mL of ε-CL with 0.113 g of hexanoic acid as initiator under argon and mechanical stirring at 240°C for 7 h. The polymer was precipitated three times in methanol and filtered and dried for 12 h under vacuum.

Chloride oligomers

Dried oligomer (0.25 g) was dissolved in $CHCl_3$ (5 mL). A 2 eq. of thionyl chloride was added under argon and the mixture was maintained under stirring for 2 h. The solvent was evaporated by increasing the argon flow. The Cl-oligomer obtained was dried under vacuum (10 mmHg) for 1 h at 100°C and then dissolved in $CHCl_3$. The solvent was evaporated and the Cl-oligomer was dried under vacuum for another 1 h.

Grafting of oligomers onto cellulose film

A 0.2 mL of the solution of chloride oligomers was deposited onto a paper sheet of 1.5×4 cm^2 size previously predried 4 h at 105°C. The paper sheet was treated for 12 h at different temperatures. The grafted paper was washed five times with 25 mL of CH_2Cl_2 at 80°C for 2 h to remove adsorbed polymer from the surface.

Grafting of oligomers onto cellulose powder

A 5 mL of a 10 g L^{-1} solution of chlorinated oligomers was poured into 1 g of predried microcrystalline cellulose. The cellulose powder was heated for 1 h at the 65°C up to 105°C. The powder was washed with 25 mL of CH_2Cl_2 at 80°C and then filtrated. This step was repeated five times yielding to 0.80 g of powder. Before contact angle measurement grafted cellulose powder was heated up to 110°C and pressed at 150 bars during 1 min to form film.

Characterization

Measurements of molar masses

Average molar masses were determined by SEC using a Kontron 420 pump with two styragel columns PL gel mixte C, 5 μm from polymer laboratories connected in series, and a Shodex RI-71 model refractive index detector. The system was calibrated by using polystyrene standards of low polydispersity index purchased from Polysciences M_n (in g mol^{-1}): 2,656,000, 841,700, 320,000, 148,000, 59,500, 28,500, 10,850, 2,930, and 580. The samples were dissolved at a concentration of 10 mg mL^{-1} in $CHCl_3$ or THF. Aliquots of 50 μL of the polymer solution were chromatographed with pure $CHCl_3$ or THF as the solvent phase at a flow rate of 1.0 mL min^{-1}.

Differential scanning calorimetry

Samples of 8–12 mg of polymers were weighed into aluminum pans and analyzed using a DSC-2010 TA instrument. The samples were scanned from −30 to 190°C with a heating rate of 20°C min^{-1} then cooling at −30°C, and scanned again from −30 to 190°C with a heating rate of 20°C min^{-1}. PCL and PHO were scanned from −90 to 190°C. The glass

transition temperature (T_g) was taken as the midpoint of the transition, in the second heating run. Melting temperature (T_m) was taken as the summit of the melting peak and the melting enthalpy (ΔH_m) was calculated from the area of the endothermic peak after the first run.

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectra were recorded on a Bruker 400 spectrometer at room temperature. Chemical shifts were given in parts per million ppm relative to the signal of chloroform as internal reference (^{1}H NMR, 7.27 ppm; ^{13}C NMR, 77.7 ppm). Quantitative ^{13}C NMR measurements were carried out by using a sequence with a pulse of 30°, an acquisition time of 2.7 s, and a delay of 6 s between scans. The quantitative ^{13}C NMR spectra were recorded in the inverse gated mode.

Fourier transform infra red spectroscopy

FTIR spectra were recorded with Brucker Tensor 27 with 32 scans, by Attenuated Total Reflectance for solid sample, and by FTIR for solution polymer between two pellets of KBr using chloroform as reference.

Contact angle measurement

The equilibrium water CA was measured by a contact angle measurement system (EasyDrop DSA15S, Krüss) at room temperature. A 10-μL droplet of deionized water was applied onto the cellulose surface with a syringe. The contact angle on each sample was measured at five different points.

Thermal gravimetric analysis

TGA experiments were performed on Setsys Evolution, SETARAM, from 20 to 500°C at 10°C min^{-1}. Ten milligram of product was used for each experiment. All TGA runs were performed under argon.

Scanning electronic microscopy

SEM observations were carried out using a LEO 1530, Carl Zeiss, Thornwood, NY. An accelerating voltage of 3 kV was used. The samples were coated with palladium-platinum before observation.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy characterization of the polymers of interest was achieved with a Cameca MAC II analyzer operating in the constant analyzer energy mode. The best nominal energy resolution of 1.0 eV (10 eV pass energy) is applied for C-1s, O-1s window spectra while a 2.5 energy resolution (37.5 eV pass energy) is chosen to record widescan spectra produced by the Al Kα anode of the dual Al-Mg unmonochromated X-ray source (230 W, 57° mean incidence angle). Calibration of the spectrometer energy scale is performed acquiring on a pure copper sample Auger and XPS spectra of well referenced energies (MVV and LVV Cu Auger energy transitions respectively, at 62.30 and 918.62 eV kinetic energy, XPS Cu-2$p_{3/2}$ and 3p photopeaks at 932.67 and 75.14 eV binding energy.

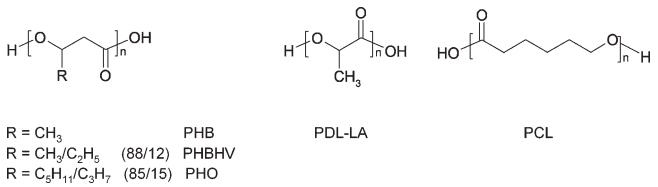

Figure 1 Formula of polyesters used.

RESULTS AND DISCUSSION

The interactions between carboxylic groups of polyesters and hydroxyl groups of cellulose are not sufficient to create a good polymer/fibers interface in the resulting biocomposites. The aim of this study is to graft onto cellulose different oligoesters: PHB, poly(3-hydroxybutyrate-*co*-hydroxyvalerate), PHBHV, poly(3-hydroxyhexanoate-*co*-hydroxyoctanoate), PHO, PDL-LA, and PCL (Fig. 1).

Preparation of PHA oligomers by thermal treatment

Various methods were developed for preparing low molar masses poly(3-hydroxyalkanoates) like acid catalyzed methanolysis,[24–26] transesterification reaction,[27–29] and thermal degradation.[30,31] The oligomer end groups were dependent on the chosen method. In this study, a reactive carboxylic end group was needed so PHAs oligomers were prepared by thermal treatments. Considering PCL oligomers, ring opening polymerization from ε-caprolactone was applied using hexanoic acid as initiator. P(DL-LA) was provided by Galactic. After thermal treatment, PHB oligomers had a carboxylic group at one side and an unsaturated group on the other side resulting from a cis elimination reaction. The reactions were stopped at different times. As shown in Table I, the molar masses of PHAs oligomers were controlled by adjusting the reaction times. The thermal treatment was allowed to proceed for 15–75 min to produce PHB oligomers with molar masses from 17,100 to 1100 g mol^{-1}. Figure 2 represented the $1/P_n$ values as a function of time (P_n is the number average degree of polymerization at time t). The inverse of P_n is a linear function of reaction time and consequently the scission rate is independent of the molar mass and of the position of the scission on a

TABLE I
Characterization of PHA Oligoesters PDL-LA and PCL

Polymer	T (°C)	t (min)	Yield (%)	M_n[a]	M_n[b]	I_p	T_g (°C)	T_m (°C)
PHB	–	–	–	–	144,000[b]	2.3	8	176
PHB	190	15	95	17,100	21,000[b]	2.4	6	172
	190	20	96	6600	15,100[b]	2.4	4	170
	190	30	94	3500	5500[b]	2.5	−2	161
	190	75	92	1100	2400[b]	2.4	−6	149
PHBHV	–	–	–	–	87,000[b]	1.9	8	158
PHBHV	190	60	99	5400	11,000[b]	1.7	−4	147
PHO	–	–	–	–	67,000[c]	1.8	−40	55
PHO	200	120	99	21,900	18,300[c]	1.9	−40	51
PCL	–	–	–	6000	12,100[c]	1.5	−60	63
PDL-LA	–	–	–	1000	760[c]	3	16	–

[a] Determined by ^{1}H NMR.
[b] Determined by SEC in CHCl3.
[c] Determined by SEC in THF.

given chain.[32] Thermal resistance of PHO was higher than PHB, due to the presence of long pendant side chain. To increase the rate of PHO oligomer preparation, the thermal treatment was made at 200°C.

The chemical structure of PHAs oligomers were confirmed by ^{1}H (Fig. 3) and ^{13}C NMR. The signals of the methyl, methylene, and methyne protons of the PHB units are detected at δ 1.2 ppm (HB_4), 2.5 ppm (HB_2), 5.2 ppm (HB_3). In addition to these signals, three signals are shown at δ 1.8, 5.8, and 6.9 and they are attributed to PHA unsaturated end group. H_a and H_b are the protons in the trans configuration at 5.8 and 6.9 ppm, respectively, CH_3—CH=CH_a—COO. The methyl end group CH_3 (HB_{12}) was found at 1.8 ppm. The molar masses of PHAs were calculated on the basis of the integrations of the H_a and the CH of the backbone at 5.2 ppm. For PCL the molar masses were determined by the comparison of the integration of the CH_2—OCO at 4 ppm and the CH_3 end group at 3.6 ppm characteristic of initiator. For PLA molar mass determination, the integration of CHOH end group at 4.3 ppm was compared to the integration of COO—C**H**(CH_3) of the backbone at 5.1 ppm. As it was expected for polyesters, the molar mass determined by SEC is higher than the molar mass determined by NMR. In our further reactions we have only taken in account the molar mass determined by NMR. The reaction produced some crotonic acid, which is the end-product of thermal degradation, and some can evaporate with high temperature and argon flow, since boiling point of crotonic acid is 180°C. That can explain the decreasing in yield with reaction time for PHB. PHAs oligomers were analyzed by DSC (Table I). Values of glass transition temperatures and melting temperatures decrease with molar masses as it was expected but the oligomers were always semi crystalline.

Preparation of PCL oligomer

PCL oligomers were prepared by ROP using hexanoic acid as initiator with a theorical molar mass of 5000. The reaction was made in argon, at 240°C for 7 h. The oligomer was purified by three precipitations in methanol. The molar mass determined by NMR was 6000 g mol^{-1} (I_p = 1.5). PCL oligomer was semi crystalline (T_m 63°C, T_g −60°C).

Preparation of chloride oligomers

The formation of PLA end capped by an acid chloride in the presence of thionyl chloride was previously described by Ustariz-Peyret et al.[33] This method was used to introduce an acid chloride group at the end group of PHA, PLA, and PCL oligomers in specific experimental conditions. The formation of chloride oligomers was made with thionyl chloride in chloroform for 2 h. The reaction

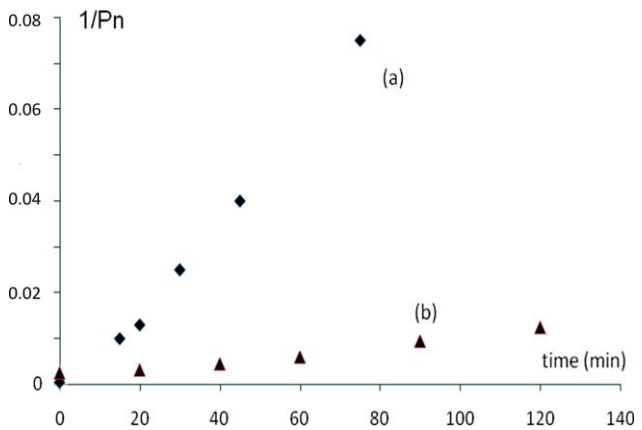

Figure 2 Evolution of $1/P_n$ (degree of polymerization) during the degradation of (a) PHB and (b) PHO at 190°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

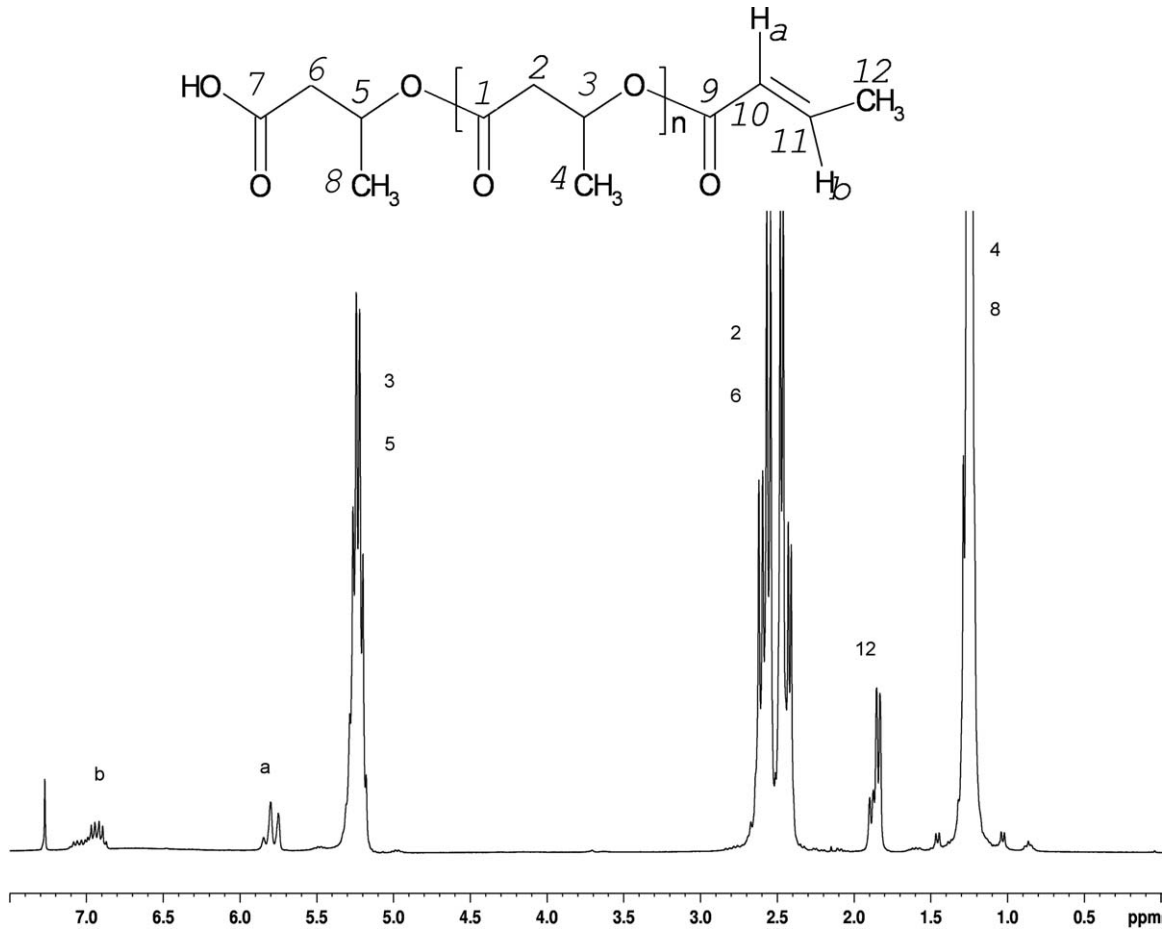

Figure 3 ^{1}H NMR ($CDCl_3$) of PHB oligomer (M_n = 1100) obtained after 75 min of thermal treatment at 190°C.

was followed by FTIR. The most prominent marker band for PHB is the ester carbonyl band near 1740 cm^{-1}. After 2 h of reaction with thionyl chloride a band at 1800 cm^{-1} has appeared as a characteristic of an acid chloride group (Fig. 4). The product was also characterized by ^{1}H NMR and ^{13}C NMR. According to the proton integration (Fig. 5), it is seen that the chloration is complete after 2 h. The two protons of the CH_2 (noted 6′) in alpha of the acyl chloride were not equivalent, and have a resonance at 3.1–3.2 ppm. The ^{13}C NMR spectrum of PHB chloride noted PHB-COCl gave information about oligomer end groups (Fig. 6). The signals at 123 ppm, noted (C=CH_a) and at 145 ppm noted

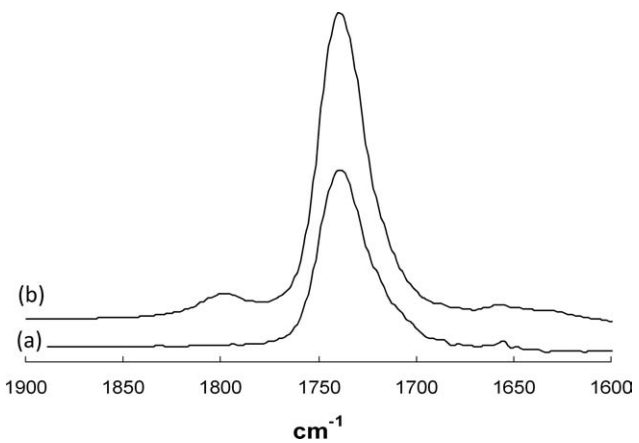

Figure 4 FT-IR (ATR) spectra of (a) PHB oligomers (b) PHB choride after reaction with thionyl chloride.

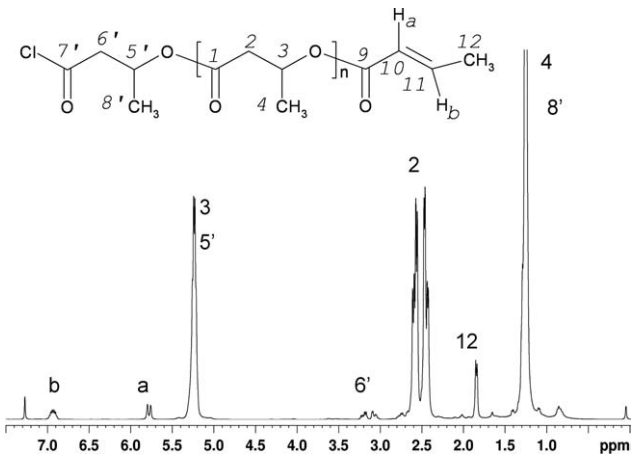

Figure 5 ^{1}H NMR ($CDCl_3$) of PHB-COCl oligomer (M_n = 1100).

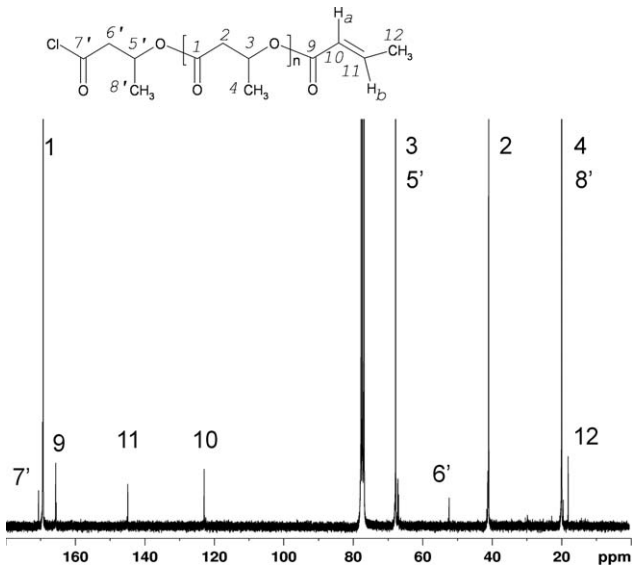

Figure 6 ^{13}C NMR ($CDCl_3$) of PHB-COCl oligomer (M_n = 1100).

(C=CH_b) were attributed to the unsaturated end group. The $\boldsymbol{CH_2}$ —COCl signal at 52 ppm, noted (6′), was here clearly distinguished and was considered as evidence for the reaction. Different peaks were observed between 169.7 and 174 ppm. The signal of the ester group of the natural PHB backbone is located at 169.7 ppm. The peak at 174 ppm attributed to free carboxylic group disappeared and a peak centered at 170.5 ppm, noted 7′ due to the choride end group appeared.

Grafting of oligoesters onto cellulose

An original and fast method was developed to graft chloride oligoesters (with molar masses from 1100 to 21,900 g mol^{-1}) on the cellulose films. The grafting reaction proceeded onto two different cellulose substrates. In the first part, the grafting reaction was made onto cellulose films containing 28% of soft wood and 71% of hard wood. In the second part, it was realized onto microcrystalline cellulose powder. Chloride oligoester, noted PHB-COCl, in solution in $CHCl_3$ at different concentrations (2–100 g L^{-1}) were deposited on dried films by a syringe. The grafting reaction was studied at different temperatures (25–105°C), during different reaction times (1–12 h). The number of deposits varied from 1 to 3. The grafting reaction was followed by gravimetry, FT-IR, XPS, and contact angle measurements.

To study the importance of the chloride group on the grafting reaction, oligoester noted PHB-COOH (M_n = 6600) without any chloride group, was deposited on the film surface and heated to 105°C. Three extractions with CH_2Cl_2 have completely removed the oligoester that was just adsorbed. No covalent link was created by esterification between PHB-COOH and cellulose in this condition. When chloride oligoesters were employed, the extractions with CH_2Cl_2 were not sufficient to remove the oligoesters that were covalently linked to the cellulose surface. After the extractions with CH_2Cl_2, the weights of grafted films were nearly the same as the initial films (Table II). Nevertheless, the hydrophobicity of films was completely different. The small quantity of grafted oligoesters was sufficient to modify the film surface. FTIR spectra of cellulose film before and after grafting are shown in Figure 7. The peak at 1640 cm^{-1} is attributed to the absorption band of the hydroxyl group of water absorbed from cellulose.[33,34] An absorption band at 1740 cm^{-1} assigned to carbonyl band of polyester is detected after grafting attesting the presence of PHB. To compare the characteristic of grafting onto cellulose the ratio of the FTIR absorbance of the C=O band at 1740 cm^{-1} to the absorbance at 1640 cm^{-1} is considered. The results are shown in Table III. For the initial cellulose film the ratio was calculated as 0.07. Even at low concentration of oligoesters (2 g L^{-1}) the FTIR ratio is above 0.07. Nevertheless the film surface is not hydrophobic. This has suggested that a certain quantity of PHB is required to make the cellulose film hydrophobic and the FTIR ratio has to be superior up to 0.13. When the grafting reaction temperature is above 65°C the grafting reaction of PHB-COCl is sufficient to change the hydrophobicity of the film. The two surfaces of the film became hydrophobic because the chloride oligoesters were dissolved in $CHCl_3$. During the deposit with the syringe on the surface of cellulose film, the solvent penetrated quickly into the film so that the second surface of the film was also in contact with chloride oligoesters. Contact angle measurements are performed to estimate the change of hydrophilicity of

TABLE II
Weights of PHB Grafted Cellulose Film Before and After Extraction with CH2Cl2

	Number of deposits	Weight (mg) after grafting	Weight (mg) after extraction with CH_2Cl_2
Natural cellulose film	–	–	228
PHB-COCl grafted cellulose	1	280	231
PHB-COCl grafted cellulose	2	328	230
PHB-COCl grafted cellulose	3	371	226

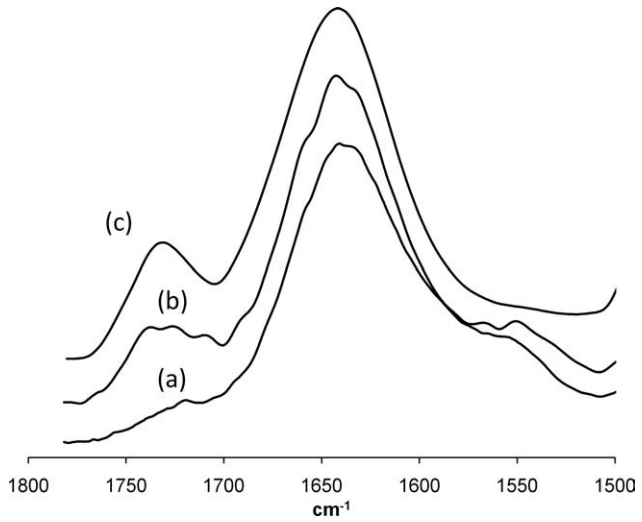

Figure 7 FTIR spectra of (a) cellulose film (b) PHB-grafted film cellulose (c) PHB-grafted powder cellulose.

TABLE III
Experimental Conditions for Grafting of PHB-COCl onto Cellulose Film

Concentration (g L^{-1})	T (°C)	t (h)	Number of deposit	A_{1740}/A_{1645}	Contact angle(°)
2	105	12	1	0.13	0
5	105	12	1	0.16	132
10	25	1	1	0.09	0
	25	12	1	0.07	0
	45	1	1	0.13	0
	65	1	1	0.21	130
	85	1	1	0.20	131
	105	1	1	0.21	132
50	105	1	1	0.20	132
	105	2	1	0.22	131
	105	3	1	0.24	131
	105	12	1	0.22	132
	105	12	2	0.18	132
	105	12	3	0.25	131
100	105	12	1	0.15	133
50[a]	105	12	1	0.07	0
50[a]	105	12	3	0.07	0

[a] PHB-COOH oligomers.

the grafted film compared to the unmodified cellulose. Figure 8 represents a water droplet deposited on the surface (a) of a PHB film obtained by solvent casting and (b) of a PHB-grafted cellulose film. The water contact angle of solvent cast PHB film was found to be 78° which was in agreement with literature,[33] whereas the contact angle is about 130° for the grafted cellulose film (Table III). This difference can be explained by the roughness of the cellulose films. To verify this hypothesis three different cellulose films are tested and the results are presented in Table IV. The results showed that the contact angle decreased (125 to 132°) with the roughness of the cellulose film (3.7 μm to 10.8) but it remains always superior to the contact angle of the PHB film, as previously described by Lönnberg et al.[22] By this method, the temperature of the reaction is the major experimental parameter because efficient grafting is obtained at reaction temperature superior or equal to 65°C. When the oligoester concentration is of 10 g L^{-1} the reaction is completed after 1 h at 65°C.

We have tested another way to graft the PHB chloride by immersing the paper sheet in a flask containing a solution of PHB-COCl in chloroform at 10 g L^{-1} during different times (1, 3, 6, and 12 h) before heating the paper sheet at 105°C during 12 h. In this case the paper exhibited a hydrophobic nature (contact angle of 125°) and FTIR ratio (A1740/1645) was about 0.14. This process does not increase the quantity of PHB grafted on the paper compared to the simple deposit method using a syringe.

By comparison grafting reaction is more efficient when powder cellulose was employed. FT-IR ratio was nearly 0.34 (Table V). However contact angle value was about 80° which is of the same order of magnitude of contact angle of pure PHB, proving that the value of contact angle depended on the porosity of the employed substrates.

Oligoester grafting was not detectable by scanning electron microscopy (photo not shown) because of the very small quantity of oligoester on the cellulose surface. The changes in the hydrophobicity of the grafted film were associated with structural changes

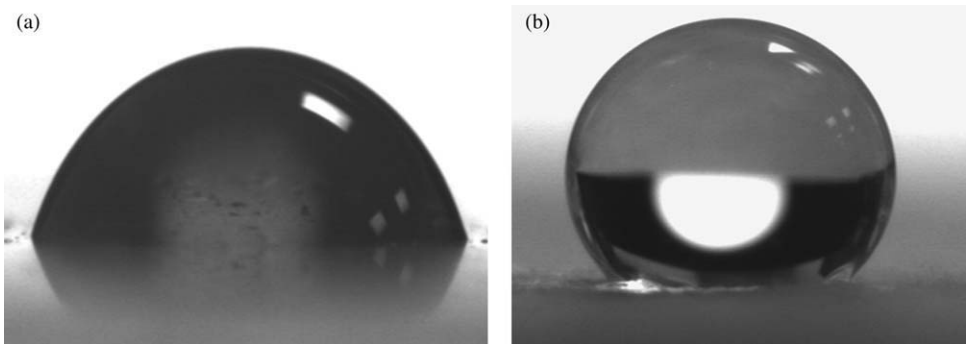

Figure 8 A water droplet deposited on the surface of (a) PHB film and of (b) PHB grafted cellulose film.

TABLE IV
Contact Angle Measurements for Different Grafted Cellulose Films

	Thickness (μm)	Density	Roughness (μm)	Contact angle (°)
PHB grafted—cellulose 1	323	0.28	10.8	131
PHB grafted—cellulose 2	123	0.74	4.7	128
PHB grafted—cellulose 3	109	0.83	3.7	125

TABLE V
Experimental Conditions for PHB Grafting onto Cellulose Powder

	T (°C)	t (h)	A_{1740}/A_{1645}	Contact angle (°)
Cellulose powder	–	–	0.03	23
PHB grafted-cellulose powder	65	1	0.25	79
	85	1	0.29	80
	105	1	0.34	81
	105	12	0.32	79

on the film surface. To investigate the effect of grafting, XPS analysis on the surface was employed. The XPS multiplex scan of a solvent cast PHB sample shows a 1 : 1 : 1 ratio of C═O : C─O : C─(C═O) peaks as expected from the structure and in agreement with previous studies.[35,36] The C1s spectrum of cellulose was resolved into three components with different bonding state: the first at 285 eV assigned to C─C or C─H bond; the second at 286.8 eV assigned to C─O bond; the third at 288 eV assigned to C═O bond. The C1s spectrum of grafted film showed considerable changes in the chemical state of C. Now the spectrum can be resolved into four components (Fig. 9). A new component appeared at an energy of 289 eV, corresponding to O─C═O bond. This peak is the characteristic of PHB attesting the presence of PHB at the cellulose film surface.

Influence of the length and nature of grafted oligoesters

PHB-COCl having different molar masses (1100, 3500, 6600, and 17,100 g mol^{-1}) have been deposited on paper surface. It was observed that the grafting did not depend on the length of PHB because all the grafted films were hydrophobic. Table VI gives the average contact angle measured with drop of water deposited on films grafted by PHB, PHBHV, PCL, PDL-LA, and PHO. The success of oligomer grafting was confirmed by FT-IR, mainly by the appearance of a new carbonyl ester band at 1740 cm^{-1}, characteristic of polyesters. The calculated ratio A1740/1645 was about 0.22. Nevertheless the hydrophobicity did not depend on the polyester nature because the contact angle obtained for different grafted films were of the same order of magnitude even when the cellulose was grafted with PDLA with a molar mass of 760 g mol^{-1}. The presence of carboxylic end group in this polymer did not affect the hydrophobicity of grafted cellulose.

Thermal stability of grafted film

Thermogravimetric analysis of PHB grafted cellulose was performed to evaluate the effect of the presence of PHB oligomer on the course of degradation. Figure 10 shows the variation of weight loss versus temperature for PHB, cellulose films, and grafted films. The initial degradation temperatures from TGA and maximum degradation temperatures from the derivative thermogravimetry (DTG) are reported in Table VII. The TGA curve of initial PHB indicated that the PHB degradation initiated at 200°C and its complete degradation occurred at 270°C. Cellulose

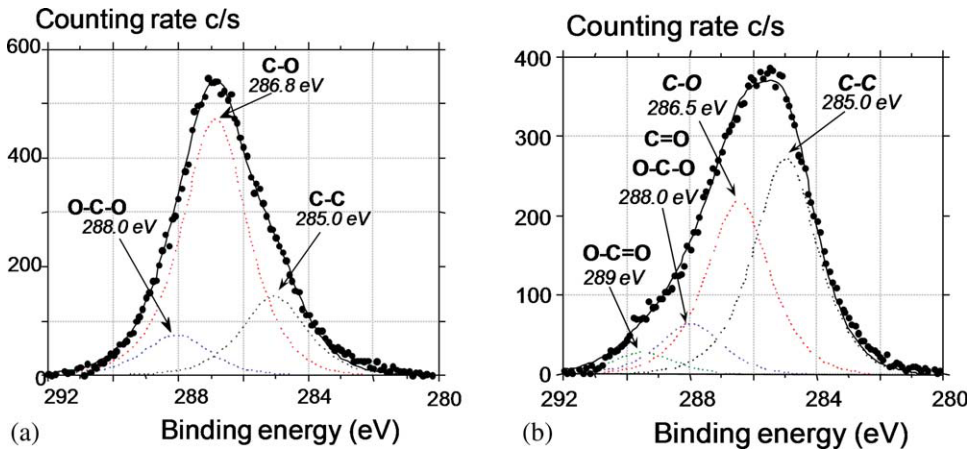

Figure 9 XPS multiplex scans of the carbon region of (a) cellulose and (b) PHB grafted cellulose film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Influence of Nature of Polyester Grafted on Cellulose Determined by Contact Angle Measurement and FTIR Spectroscopy

Polyester nature	M_n (g mol^{-1})	Contact angle (°)	A_{1740}/A_{1645}
PHBV	5400	133	0.21
PHO	21,900	129	0.24
PCL	6000	135	0.22
P(DL-LA)	1000	130	0.20
PHB	1100	129	0.21
PHB	6600	131	0.25
PHB	17,100	132	0.25

films were more stable than PHB to thermal degradation and the TGA curve indicated that the maximum degradation occurred at 370°C and onset at 240°C. After grafting reaction the quantity of the adsorbed PHB is very important (Fig. 11). The extractions with CH_2Cl_2 removed the adsorbed PHB and we just observed a shoulder at 260°C attesting the presence of PHB oligomer grafted but in a very small proportion. The grafted PHB still degraded at melt at 260°C. TGA results showed that the maximum temperature of degradation of the initial cellulose (349°C) is of the same order of magnitude than the degradation temperature of grafted cellulose (344°C).

CONCLUSIONS

In this study, different oligoesters PHB, PHBHV, PHO, PD-LA, and PCL were prepared. These oligomers were further grafted onto cellulose films through direct esterification without any catalyst. The employed method consists of deposition of oligoester chlorides on the surface of the cellulose film and is followed by a heating step at a temperature of 65°C during 1 h.

TABLE VII
Results of TGA and DTG

Polyester nature	$T_{5\%}$[a] (°C)	T_{max}[b] (°C)
PHB	234	267
PHB oligomer	210	260
Cellulose	271	349
PHB grafted cellulose	251	344

[a] $T5\%$ = temperature when the weight loss is 5%.
[b] Tmax = temperature max of DTG.

The successful grafting was confirmed by a combination of complementary experimental techniques. The presence of the oligoesters on the cellulose surface was concluded on the basis of a qualitative analysis of the XPS spectra. ATG studies have shown that the thermal stability of the films was not affected by the grafting reaction because of the small quantity of polyester grafted. Nevertheless it was sufficient to lead to a drastic change of its property, which became very hydrophobic. The important observation is that there is an increase of hydrophobicity of the two surfaces of the paper which is independent of the nature and length of grafting oligoesters. The proposed chemical modification pathway of cellulose films is of particular interest because the hydrophobic pendant grafts of the cellulose and composite matrices have chemically similar polymer backbone, namely aliphatic degradable polyesters. Further study can be made on biocomposites prepared using grafted cellulose samples and mechanical properties may be studied.

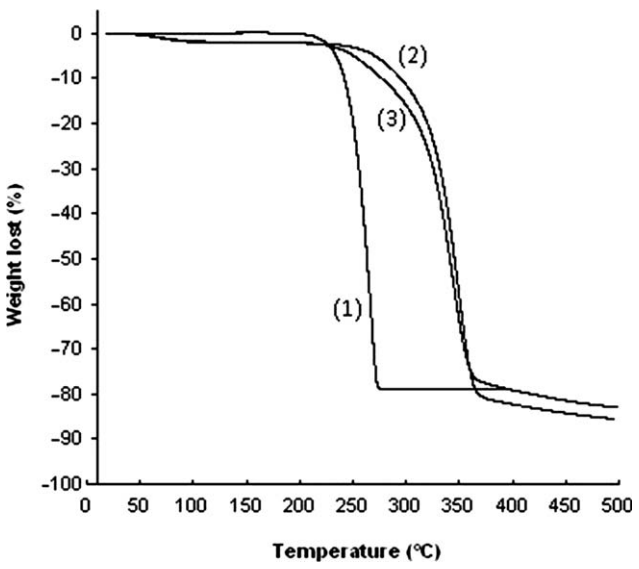

Figure 10 Thermogravimetric analysis of (1) PHB, (2) cellulose, and (3) PHB grafted cellulose film.

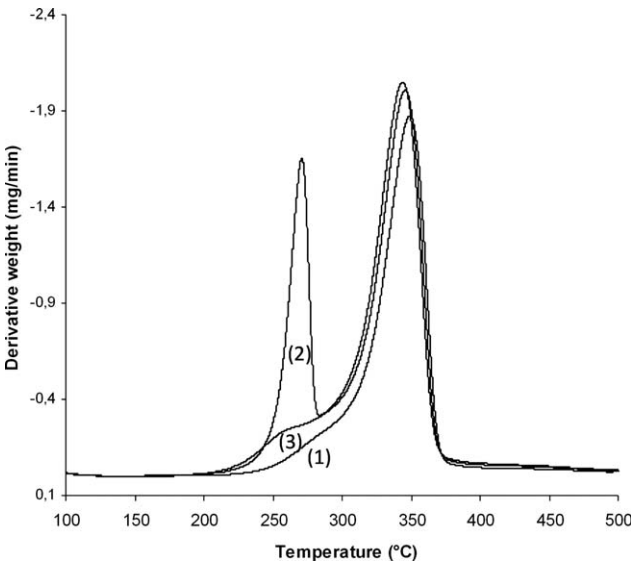

Figure 11 Thermogravimetric analysis, derivative weight. (1) Cellulose, (2) oligomer PHB-grafted cellulose before extraction, and (3) PHB-grafted cellulose after extraction.

The authors acknowledge Dr. U. Hanggi (Biomer), Dr. B. Carbonnier, Pr. Philippe Guérin (ICMPE, Thiais) for helpful discussions and Dr. P. Coszach (Galactic) for providing PDLLA. Alstrom is thanked for provided wood fibers films and for technical help.

References

1. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276/277, 1.
2. Mohanty, A. K.; Misra, M.; Drzal, L. T. J Polym Environ 2002, 10.
3. Gatenholm, P.; Kubat, J.; Mathiason, A. J Appl Polym Sci 1992, 45, 1667.
4. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Comp Sci Technol 2000, 64, 115.
5. Singh, S.; Mohanty, A. K. Compos Sci Technol 2007, 67, 1753.
6. Wong, S.; Shanks, R.; Hodzic, A. Compos Sci Technol 2004, 64, 1321.
7. Dufresnes, A.; Kellerhals, M. B.; Witholt, B. Macromolecules 1999, 32, 1396.
8. Zini, E.; Focarete, M. L.; Noda, I.; Scandola, M. Compos Sci Technol, 2007, 67, 2085.
9. Ali, R.; Iannace, S.; Nicolais, L. J Appl Polym Sci 2003, 88, 1637.
10. Plakett, D.; Andersen, T. L.; Pedersen, W. B.; Nielsen, L. Compos Sci Technol 2003, 63, 1287.
11. Oksman, K.; Mathew, A. P.; Bondeson, D.; Kvien, I. Compos Sci Technol 2006, 66, 2776.
12. Bodros, E.; Pillin, I.; Montrelay, N.; Baley, C. Compos Sci Technol 2007, 67, 462.
13. Raj, R. G.; Kokta, B. V.; Daneault, C. Makromol Chem Macromol Symp 1989, 28, 187.
14. Devi, S. U.; Bhagawan, S. S.; Thomas, S. J App Polym Sci 1997, 67, 1739.
15. Joseph, K.; Pavithran, C.; Thomas, S. Polymer 1996, 37, 5139.
16. Shanks, R. A.; Hodzic, A.; Wong, S. J Appl Polym Sci 2004, 91, 2114.
17. Lee, S. G.; Choi, S. S.; Park, W. H.; Cho, D. Macromol Symp 2003, 197, 89.
18. Wong, S.; Shanks, R. A.; Hodzic, A. Macromol Mater Eng 2002, 287, 641.
19. Chen, C.; Peng, S.; Fei, B.; Zhuang, Y.; Dong, L.; Feng, Z.; Chen, S.; Xia, H. J Appl Polym Sci 2003, 88, 659.
20. Mohanty, A. K.; Drzal, L. T.; Desai, S. M.; Misra, M.; Mulukutla, P. US Patent 0,215,672 A1, 2005.
21. Carlmark, A.; Malmstroem, E. E. Biomacromolecules 2003, 4, 1740.
22. Lönnberg, H.; Zhou, Q.; Brumer, H.; Teeri, T. T.; Malmström, E.; Hult, A. Biomacromolecules 2006, 7, 2178.
23. Dufresne, A.; Samain, E. Macromolecules 1998, 31, 6426.
24. Gross, R. A.; Mc Carthy, S. P.; Reeve, M. S. US Patent 5,439,985, 1995.
25. Marchessault, R. H.; Yu, G. Polym Prepr (Am Chem Soc Div Polym Chem) 1999, 40, 527.
26. Timbart, L.; Renard, E.; Tessier, M.; Langlois, V. Biomacromolecules 2007, 8, 1255.
27. Hirt, T.; Neuenschwander, P.; Suter, U. Macromol Chem Phys 1996, 197, 1609.
28. Andrade, A. P.; Witholt, B.; Hany, R.; Egli, T.; Li, Z. Macromolecules 2002, 35, 684.
29. Ravenelle, F.; Marchessault, R. H. Biomacromolecules 2002, 3, 1057.
30. Nguyen, S.; Yu, G.; Marchessault, R. H. Biomacromolecules 2002, 3, 219.
31. Timbart, L. Thèse Université Paris 2005, 12.
32. Jellinek, H. H. G. Degradation of Vinyl Polymers; Academic Press: New York, 1955, p 15.
33. Ustariz-Peyret, C.; Coudane, J.; Vert, M.; Boisrame, B. J Microencapsulation 2000, 17, 615.
34. Carillo, F.; Colom, X.; Sunol, J. J.; Saurina, J. Eur Polym J 2004, 40, 2229.
35. Yakimets, I.; Paes, S. S.; Wellner, N.; Smith, A. C.; Wilson, R. H.; Mitchell, J. R. Biomacromolecules 2007, 8, 1710.
36. Mas, A.; Jaaba, H.; Schue, F.; Belu, A. M.; Kassis, C.; Linton, R. W.; Desimone, J. M. Eur Polym Mater 1997, 33, 331.