Synthesis and Characterization of Compatibilized Poly(ε–caprolactone)/Granular Starch Composites

*Emmanuel Duquesne, Delphine Rutot, Philippe Degée, and Philippe Dubois**

Laboratory of Polymeric and Composites Materials, University of Mons-Hainaut, Place du Parc 20, B-7000, Belgium

SUMMARY: To improve the mechanical properties of granular corn starch-filled poly(ε-caprolactone) (PCL) compositions, three strategies were investigated including the hydrophobic coating of starch granules by reaction with n-butyl isocyanate, the addition of PCL-grafted dextran (PGD) as an amphiphilic compatibilizer, and the use of PCL-grafted granular starch (PGS). Except for the chemical modification of granular starch by reaction with n-butyl isocyanate, the synthesis of both PGD and PGS relies upon the controlled ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by Al-alkoxides generated onto the polysaccharide, either dextran or starch particles. While the hydrophobic coating of starch only provides higher tensile strength and elongation at break, these properties as well as Young's modulus and strength at yield of the PCL/starch blends were remarkably increased by locating the PCL-grafted dextran at the filler/matrix interface. It is however worth pointing out that a tougher and stiffer material was obtained by melt blending PGS and pure PCL. These property changes were analyzed and clearly related to parameters such as filler dispersion, interfacial tension, interfacial adhesion and reinforcement by PCL crystallites.

Introduction

Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. However, starch-based plastics have some drawbacks, including limited long-term stability caused by water absorption, poor mechanical properties and processability. In order to solve some of these problems, various physical or chemical modifications of starch have been considered, including chemical derivatization, graft copolymerization and blending. Since Griffin prepared starch-filled compositions[1)], several kinds of starch/synthetic polymer blends have been developed[2)]. However, these blends could not be useful as biodegradable plastics because they contained non-degradable component. For preparing completely biodegradable blends, starch has been blended with aliphatic polyesters such as poly(ε-caprolactone) (PCL)[3-5)]. These studies showed that the mechanical properties of the PCL/starch blends made from various types of starch generally become

 CCC 1022-1360/00/$ 17.50+.50/0

poorer with increasing starch content. This can be attributed to the incompatibility between the hydrophobic PCL and the hydrophilic starch. Thus, it is expected that the properties of the PCL/starch blend could be improved by using the proper compatibilizer, which can induce the enhancement of both interfacial tension and adhesion between the separate phases [6-9].

This paper aims at examining different methods to increase the compatibility of PCL/granular starch compositions. In a first series of experiments, starch granules were coated with a hydrophobic organic layer before melt blending with PCL. Secondly, PCL-grafted dextran was synthesized and added as a compatibilizer to PCL/starch compositions. Finally, starch granules were encapsulated by an *in situ* grown and covalently bound PCL shell and then melt blended with pure PCL to reach a define composition. The effect of these modifications on the interface of PCL/starch blends was analyzed from their tensile properties and their morphology as observed by scanning electron microscopy (SEM).

Experimental

Materials and blends preparation

Commercial grade PCL CAPA 650 was purchased from Solvay. PCL number average molecular weight (Mn) was 49,000 for a polydispersity of 1.4 as determined by size exclusion chromatography (SEC) in THF. Granular corn starch (amylose/amylopectin = 30/70; wt/wt) with a mean diameter of 13.5 μm was supplied by BioPlastics Inc. n-Butylisocyanate from Acros and dibutyltin dilaurate solution in toluene from Aldrich were used without any further purification. PCL/starch compositions were prepared by mechanical kneading on a two-roll mill at 130°C for 15 min. Then, they were molded into 3 mm thick sheets by hot-pressing at 100°C under 30 bars for 30 seconds and by cold-pressing at 15°C under 30 bars for 5 minutes. The specimens for tensile and impact measurements were cut from the sheets using a cutting press.

The hydrophobic coating of granular corn starch was made by reacting the available hydroxyl groups at the starch surface with n-butylisocyanate. In a typical experiment, 1.05g of corn starch was suspended in 4 ml of n-butylisocyanate, added with 2 ml of a dibutyltin dilaurate solution in toluene (0.01M) and reacted under stirring at 50°C for 72h. Coated starch granules were recovered by filtration, washed with THF and dried under reduced pressure until

constant weight. In an alternative procedure, thermal heating was replaced by a microwave treatment (400 W) for 5 minutes in the absence of catalyst.

The three-step synthesis and characterization of PCL-grafted dextran copolymers (PGD) was already described in details in a previous paper[10]. Typically, 9.38g of previously dried dextran T10 (from Pharmacia Biotech; Mn = 6,600) was dissolved in 100 ml of dried dimethylsulfoxide in a dried and nitrogen purged round bottom two-necked flask equipped with a stopcock and connected to an oil valve for removal of volatile. Once dextran was totally dissolved, 146 ml of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) was added. The reaction was carried out at 50°C for 20 h. In the course of the reaction, 60 ml of dried THF were added to maintain the solubility of reagents and products. Silylated dextran was recovered by precipitation into heptane, filtration and drying. In a second step, 13.76g of partially silylated dextran containing 9.06 mmol of free remaining hydroxyl groups was dried by three azeotropic distillations of toluene, then dissolved in 150 ml of dried toluene and added with 0.8 ml of a triethylaluminum solution in toluene (0.55M). After 4h and complete ethane evolution, 32 ml of dried ε-caprolactone (CL) was added and the reaction medium was heated up to 60°C for 70h. The silylated graft copolymer was recovered by precipitation in heptane, filtration and drying. Deactivation of aluminum alkoxide growing sites and deprotection of silylated dextran hydroxyl groups were carried out by dissolution in THF and addition of 1 ml of an aqueous HCl solution (1M). The *in situ* precipitated PCL-grafted dextran (PGD1) was recovered by filtration and drying. A weight fraction in PCL (F_{PCL}) of 0.65 and average degree of polymerization (DP) of 13 were determined. Two other samples were also prepared from dextran T10 with a F_{PCL} of 0.60 for a DP of 13 (PGD2) and a F_{PCL} of 0.90 for a DP of 20 (PGD3), respectively.

The PCL-grafted starch particles were obtained by *in situ* ROP of CL in the presence of granular starch as previously described by some of us[11,12]. Typically, 19.5 ml of CL was added to 20.05g of corn starch (50/50 by weight) in a 50 ml round bottom flask previously purged with nitrogen, and equipped with a stirrer and an oil valve for removal of volatile. 13 ml of triethylaluminum in toluene solution (0.53M) was then introduced under nitrogen and the reaction medium was then heated up to 90°C for 10 minutes. The polymerization was ended up by fast cooling to room temperature. Weight fraction in grafted PCL (F_{PCL}) was determined by gravimetry after selective extraction in toluene of the non grafted PCL chains. F_{PCL} was of 4% for a monomer conversion of 80% (PGS1). In an alternative procedure, starch and triethylaluminum were reacted in toluene suspension at r.t. for 2h, then toluene was evaporated and CL was added. F_{PCL} reached 24% for a monomer conversion of 96% (PGS2).

Characterization

Tensile tests were performed at 20°C by using a Lloyd apparatus with a constant deformation rate of 50 mm/min on dumbbell specimens cut in accordance to ASTM D638 V standard. IZOD and CHARPY impact tests were carried out at 20°C with a Ray-Ran pendulum on specimens cut and notched in accordance to the ASTM D256 B standard. Scanning electron micrographs were taken on a gold coated fractured surface of the dumbbell specimens using a JEOL 6100 apparatus. FTIR spectra were recorded using a BIO-RAD Excalibur spectrometer equipped with a ATR Harrick Split Pea^{TM}.

Results and discussion

Impact strength and tensile properties such as Young's modulus (E), strength at yield (σy), strength at break (σb) and elongation at break (εb) have been evaluated for PCL/granular starch compositions with starch content lower or equal to 50 wt%. Higher contents in starch are responsible for the formation of very brittle materials highly difficult to melt process. The mechanical properties are summarized in Table 1. From these data emerges that PCL, as well known, is quite a ductile polymer, able to undergo large deformations. Unfortunately, it possesses a relatively low elastic modulus making it useless for any applications where a high rigidity is required. Thus, addition of starch fillers into PCL can contribute to improve its modulus. As a matter of fact it is observed that starch granules increase effectively the Young's modulus with regard to pure PCL, but also reduce significantly all the other mechanical properties. Such a behavior results from the poor filler/matrix interfacial adhesion as evidenced by SEM observations of the fracture surface of tensile dumbbell specimens (Figure 1). The presence of a continuous void around the filler surface actually attests for the poor interfacial adhesion. Consequently, upon stress the fracture propagates at the filler surface at about an equatorial location, with some starch particles kicked away form the fracture surface.

PCL/starch blends composition was confirmed by selective extraction in toluene. SEC analysis of recovered PCL chains showed that melt blending did not detrimentally affect PCL molecular weights nor broadened the molecular weight distribution. The degree of crystallinity of the blends was also determined by differential scanning calorimetry and calculated as the ratio $\Delta H/\Delta H_0$ (where ΔH is the melting enthalpy of PCL in the samples,

while ΔH_0 refers to the value for perfect PCL crystal, i.e. ΔH_0 = 136 J/g [8]. It results that the degree of crystallinity of PCL matrix is not significantly modified by the addition of the filler ($\Delta H/\Delta H_0$= 54 +/- 3%).

Table 1: Mechanical properties of PCL/starch blends

PCL/starch (wt %)	σ_b (MPa)	ε_b (%)	Young's modulus (MPa)	σ_y (MPa)	Impact strength (IZOD) (kJ/m^2)	Impact strength (CHARPY) (kJ/m^2)
50:50	9.3	315	280	8.0	1.5	1.7
60:40	12.1	360	265	9.0	1.7	1.8
70:30	15.7	440	250	10.0	2.6	2.8
80:20	20.0	480	220	11.7	4.3	5.8
90:10	27.0	600	215	14.1	5.5	7.0
100:0	48.1	1370	210	16.0	16.0	-[a]

a) fracture could not be observed

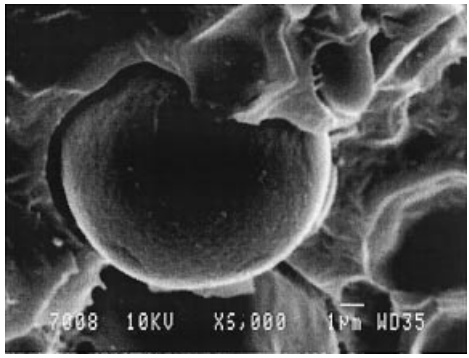
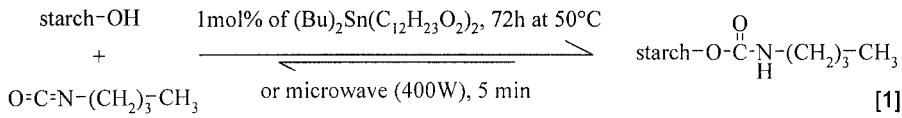


Figure 1: SEM micrograph of the surface fracture of PCL/granular starch (60:40) composition

Hydrophobic coating of starch particles

In a first series of experiments, available hydroxyl groups at the starch surface have been reacted with n-butylisocyanate (Equation 1). The reaction has been carried out either in the presence of dibutyltin dilaurate as a catalyst at 50°C for 72 hours, or without any added catalyst by using microwave (400W) for 5 minutes in a conventional oven.



[1]

FTIR spectroscopy gives evidence for the efficiency of the hydrophobic coating of starch particles (Figure 2). FTIR spectra of native and coated starch show that the decrease in relative intensity of the hydroxyl band around 3300 cm^{-1} with regard to the C-H stretching absorption is more pronounced when microwaves are used for promoting the reaction.

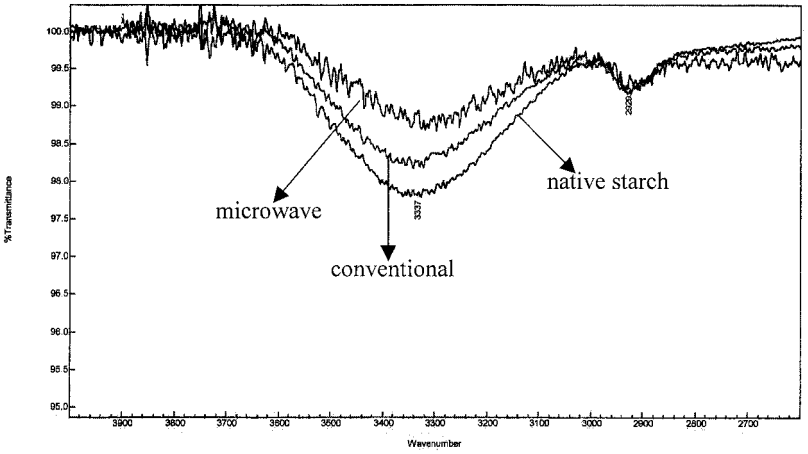


Figure 2: FTIR spectra of native and coated starch (see Eq. 1)

After chemical modification, the coated starch particles have been melt blended with PCL so as to reach a final PCL/starch composition of 30:70, and the tensile properties have been measured (Table 2). Hydrophobic coating of starch surface endows the PCL/starch composition with higher tensile stress and elongation at break, while the Young's modulus and the strength at yield are slightly reduced. These results are consistent with a better interfacial tension between the two phases meaning that the material is more homogeneous and less brittle, but also less elastic.

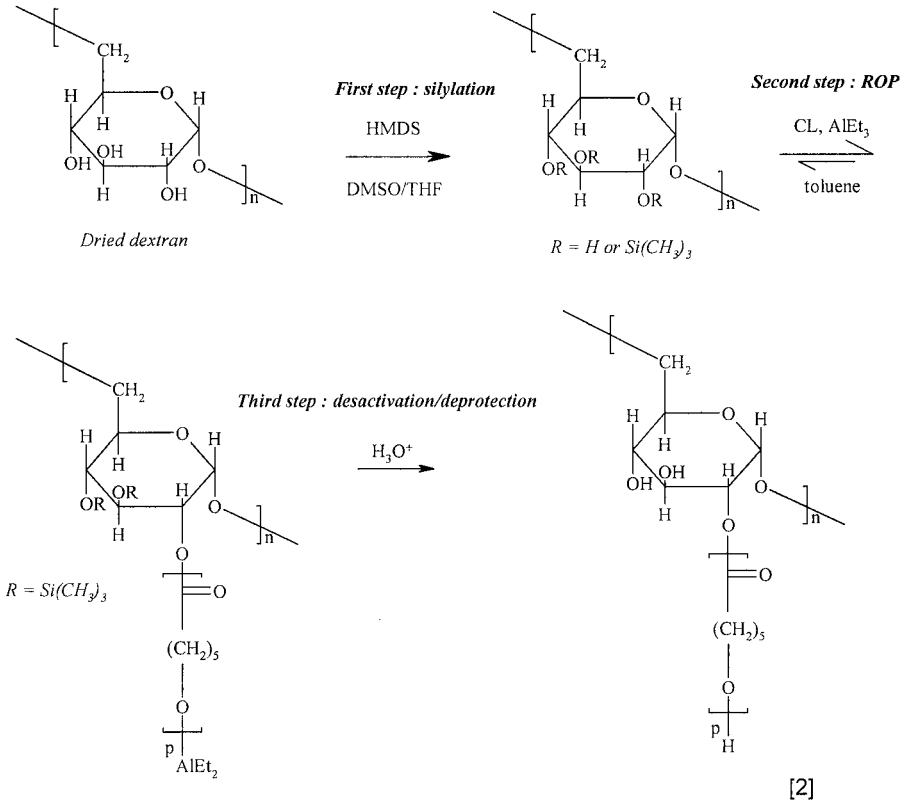
Table 2: Tensile properties of PCL/starch blends after starch coating by n-butyl isocyanate

Composition	σ_b (MPa)	ε_b (%)	Young's modulus (MPa)	σ_y (MPa)
PCL/starch (70:30)	15.7	440	250	10.0
PCL/coated starch (70:30)	18.0	530	235	8.8

Synthesis and addition of PCL-grafted dextran as a compatibilizer

In order to synthesize a wide range of PCL-grafted dextran copolymer compositions, a totally controlled three-step procedure has been developed that involves the reversible silylation of the hydroxyl groups of dextran, a water soluble polysaccharide backbone, followed by the

ring-opening polymerization (ROP) of CL initiated by the free remaining hydroxyl groups of partially silylated dextran converted into Al alkoxides functions, and finally the polysaccharide hydroxyl deprotection under mild conditions (Equation 2)[10].



The high efficiency of grafting and the control over the grafts molecular weight and molecular weight distribution rely upon the well-known "living" nature of the coordination-insertion mechanism of the ROP that is initiated by aluminum alkoxides[13]. Accordingly, the free hydroxyl groups remaining along the polysaccharide backbone have been activated by using either $Al(Et)_3$ or $Al(O^iPr)_3$ in catalytic amount ([OH] /[Al]=20) so that aluminum alkoxides are made available and can interchange quickly with free remaining hydroxyl groups, compared to the propagation rate. In practice, three PCL-grafted dextran (PGD) copolymers have been synthesized with the following characteristics : PGD1 with F_{PCL} = 0.65 and DP = 13, PGD2 with F_{PCL} = 0.60 and DP = 13 and PGD3 with F_{PCL} = 0.90 and DP = 20 (where

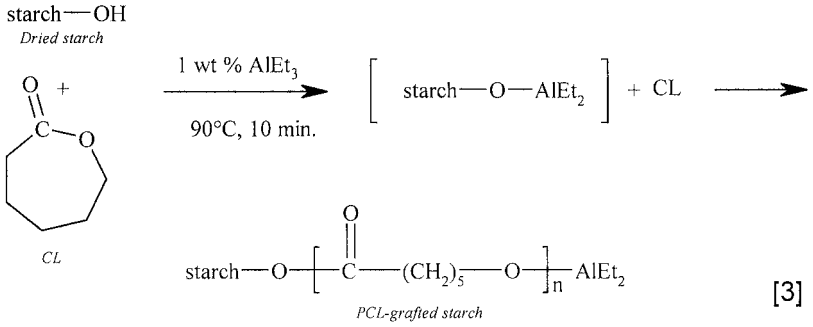
F_{PCL} is the weight fraction in PCL and DP is the average degree of polymerization of PCL grafts). In a first series of experiments, various amounts of PGD1 have been added first to molten PCL on a two-roll mill at 130°C, followed then by the addition of starch granules. Under such melt processing conditions, tensile properties were not improved. Indeed, whatever the amount of PGD1 added (from 2.5 up to 15.0 wt%), tensile stress and elongation at break of PCL/starch (60:40) blends significantly decreased, while Young's modulus slightly increased. Such a behavior could be explained by the low diffusion rate of the PGD1 copolymer within the polyester matrix rendering it unable to seat at the interface between PCL and starch. It would rather form additional separate phases composed of a dextran core and a grafted PCL shell dispersed into the polyester matrix. Credit to such an assumption has been given by melt blending PGD1 (5 wt%) directly within pure PCL. Compared to PCL alone, the tensile properties were again negatively affected : σ_b and ε_b decreased, while E increased. In order to overcome such a drawback, two different melt blending strategies have been investigated : i) PGD2 has been first melt blended with starch before PCL addition, and ii) PGD3 has been precipitated at the surface of starch before melt blending with PCL. Precipitation of the copolymer onto filler particles has been carried out by dissolving the copolymer into a toluene suspension of starch and then adding drop by drop a poor solvent of the grafted copolymer, i.e., heptane. Table 3 illustrates the tensile properties of PCL/starch (60:40) blends added with 5 wt% of PGD2 and PGD3 following the two aforementioned procedures. Interestingly, these compatibilized compositions displayed improved ultimate stress and elongation at break but also enhanced Young's modulus and strength at yield. This means that PGD2 and PGD3 do not only promote a better dispersion and a lower interfacial tension but they also contribute to reinforce the adhesion between the filler and the matrix. These observations are contrasting with the effect of PCL-grafted starch copolymers bearing short polyester sequences (DP < 5)[6]. Longer PCL grafts (DP > 13) are more likely able to interact closely with the polyester matrix while hydrogen bonding maintains dextran and starch close together. It results a stiffer and tougher composite material.

Table 3: Tensile properties of PCL/starch (60:40) blends added with 5 wt% of PCL-grafted dextran

Composition	σ_b (MPa)	ε_b (%)	Young's modulus (MPa)	σ_y (MPa)
PCL/starch (60:40)	12.1	360	265	9.0
PCL/starch/graft copo (F_{PCL}=0.6)	13.6	420	310	10.5
PCL/starch/graft copo (F_{PCL}=0.9)	13.2	400	290	10.5

In situ PCL grafting onto starch granules

The great efficiency of aluminum alkoxides as initiators in ROP of CL has been extended to the synthesis of valuable biodegradable compositions of corn starch and PCL (Equation 3)[12]. The ROP of CL has been carried out in bulk (without solvent) from previously dried starch using the amylose/amylopectine hydroxyl functions after adequate activation into Al-alkoxides. These aluminum alkoxides have been *in situ* generated by reaction of triethylaluminum with the hydroxyl functions available at the starch surface. XPS analysis has attested for the actual fixation of the aluminum active species on the starch surface, while growth of the polyester chains has been followed by laser light scattering granulometry[11].



[3]

In this study, two compositions of PCL-grafted starch (PGS) have been prepared which possess a weight fraction in PCL of 4 (PGS1) and 24 % (PGS2), respectively (see experimental section). As the grafting efficiency does never reach unity but rather lies between 0.50 and 0.95 depending on the polymerization conditions, free PCL chains contained in PGS1 have been selectively extracted by selective dissolution in toluene at r.t. for 24h. PGS2 has been used without any extraction except for an aliquot which enables to determine the number average molecular weight of free PCL chains (Mn = 60,000). In a next step, PGS1 and PGS2 have been melt blended with pure PCL in order to reach a final PCL/starch composition of 60:40.

Table 4 clearly shows that all the tensile properties have been improved by the grafting of PCL chains at the starch surface, e.g., strength at yield passes from 9.0 MPa to 16.1 MPa with PGS2. This value is very close to the one observed for pure PCL (σ_y = 16.0 MPa), while the rigidity of the composites is remarkably enhanced (E = 320-360 Mpa). As both modulus and strength are properties closely related to the hard domain fraction in the material, it is interesting to distinguish starch phase and crystalline PCL as potential hard domains in these blends.

Table 4: Tensile properties of PCL/starch (60:40) blends made from PCL-grafted starch and pure PCL

PCL/starch (60:40) composition	σ_b (MPa)	ε_b (%)	Young's modulus (MPa)	σ_y (MPa)
PCL/starch	12.1	360	265	9.0
PCL/PCL-grafted starch (F_{PCL} = 0.04)	12.5	380	360	13.0
PCL/PCL-grafted starch (F_{PCL} = 0.24))	14.5	350	320	16.1

However, because the starch content of these blends is kept equal to 40 wt%, the crystalline region of PCL is the hard domain fraction that is likely increased. In other words, the entanglement of PCL chains from the matrix and the PCL grafts available at the filler surface (PGS) does not only contribute to increase the interfacial adhesion and elasticity as evidenced by the enhancement in the stress at yield, but it should also favor the crystallization of PCL in the direct vicinity of starch granules, accordingly increasing the rigidity. SEM analysis confirms the very good interfacial adhesion created between PCL and starch through the grafting of long PCL segments onto starch particles (Figure 3).

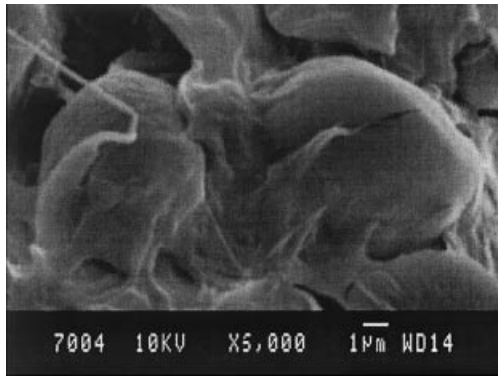


Figure 3: SEM micrograph of the surface fracture of PCL/starch blend added with PCL-grafted starch (see Table 4)

Conclusion

Tensile properties of PCL/granular starch compositions compatibilized by various methods were investigated and structural implications of the compatibilizers on the composites properties were analyzed. As expected, conventional melt blends of highly hydrophilic native

starch and hydrophobic PCL result in a significant decrease of all tensile properties except Young's modulus. Enhancement of stress and elongation at break without improvement of Young's modulus and yield stress may account for an improvement of the compatibility in terms of homogeneity of phase dispersion and better interfacial tension, as exemplified by the effect of coating starch granules by a grafted hydrophobic layer. Effective improvement of all properties could be achieved by using amphiphilic PCL-grafted dextran copolymers which are able to promote a better interfacial adhesion and thus to provide a tougher material. *In situ* ring-opening polymerization of ε-caprolactone from hydroxyl functions available at the starch surface after adequate activation into Al alkoxides is presented as a valuable way to overcome the main drawbacks of graft copolymers (three-step synthesis and precise location at the filler/matrix interface). The control of structural parameters such as the weight fraction in PCL, and the length and number of grafts, helps to govern the intermolecular interactions and subsequently the interfacial adhesion and toughness. Last but not least, it also enables to increase the fraction in hard domain and thus the rigidity of the composites.

Acknowledgments: This work was supported by the *Région Wallonne* and the *Fonds Social Européen* in the frame of *Objectif 1-Hainaut: Materia Nova*

References

1. G.J.L. Griffin, *Am Chem. Soc. Div. Org. Coat. Plast. Chem.* **33(2)**, 88, (1973)
2. P.L. Nayak, *J. Macromol. Sc.- Rev. Macromol. Chem. Phys.* **C39(3)**, 481, (1999)
3. M.F. Koening, S.J. Huang, *Polymer* **36(9)**, 1877, (1995)
4. H. Pranamuda, Y. Tokiwa, H. Tanaka, *J. Environ. Polym. Degrad.* **4**, 1 (1996)
5. L. Averous, L. Moro, P. Dole, C. Fringant, *Polymer* **41**, 4157 (2000)
6. E-J. Choi, C-H. Kim, J_K. Park, *J. Polym. Sc. Part B: Polym. Phys.* **37**, 2430 (1999)
7. E-J. Choi, C-H. Kim, J-K. Park, *Macromolecules* **32**, 7402 (1999)
8. M. Avella, M.E. Erico, P. Laurienzo E. Martuscelli, M. Raimo, R. Rimedio, *Polymer* **41**, 3875 (2000)
9. R. Mani, J. Tang, M. Battacharya, *Macromol. Rapid. Commun.* **19**, 283 (1998)
10. I. Idens, D. Rutot, Ph. Degée, Ph. Dubois, *Macromolecules*, in press
11. D. Rutot, Ph. Degée, R. Narayan, Ph. Dubois, *Composites Interfaces*, in press
12. Ph. Dubois, M. Krishnan, R. Narayan, *Polymer* **40**, 3091 (1999)
13. D. Mecerreyes, R. Jérôme, Ph. Dubois, *Adv. Polym. Sci.* **147**, 1 (1999)