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Daniel Pasquini, Eliangela de Morais Teixeira, Antonio Aprigio da Silva Curvelo, Mohamed Naceur Belgacem, Alain Dufresne. Surface esterification of cellulose fibres: Processing and characterisation of low-density polyethylene/cellulose fibres composites. *Composites Science and Technology*, 2009, 68 (1), pp.193. 10.1016/j.compscitech.2007.05.009 . hal-00524472

**HAL Id: hal-00524472**

**<https://hal.science/hal-00524472>**

Submitted on 8 Oct 2010

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## Accepted Manuscript

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PII: S0266-3538(07)00218-7  
DOI: [10.1016/j.compscitech.2007.05.009](https://doi.org/10.1016/j.compscitech.2007.05.009)  
Reference: CSTE 3709

To appear in: *Composites Science and Technology*

Received Date: 7 February 2007  
Revised Date: 28 April 2007  
Accepted Date: 5 May 2007

Please cite this article as: Pasquini, D., de Morais Teixeira, E., da Silva Curvelo, A.A., Belgacem, M.N., Dufresne, A., Surface esterification of cellulose fibres: Processing and characterisation of low-density polyethylene/cellulose fibres composites, *Composites Science and Technology* (2007), doi: [10.1016/j.compscitech.2007.05.009](https://doi.org/10.1016/j.compscitech.2007.05.009)

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**Surface esterification of cellulose fibres: Processing and characterisation of low-density polyethylene/cellulose fibres composites.**

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**Abstract**

Low-density polyethylene was filled with cellulose fibres from sugar cane bagasse obtained from organosolv/supercritical carbon dioxide pulping process. The fibres were also used after chemical modification with octadecanoyl and dodecanoyl chloride acids. The morphology, thermal properties, mechanical properties in both the linear and non linear range, and the water absorption behaviour of ensuing composites were tested. The evidence of occurrence of the chemical modification was checked by X-ray photoelectron spectrometry. The degree of polymerisation of the fibres and their intrinsic properties (zero tensile strength) were determined. It clearly appeared that the surface chemical modification of cellulose fibres resulted in improved interfacial adhesion with the matrix and higher dispersion level. However, composites did not show improved mechanical performances when compared to unmodified fibres. This surprising result was ascribed to the strong lowering of the degree of polymerisation of cellulose fibres (as confirmed by the drastic decrease of their zero tensile strength) after chemical treatment despite the mild conditions used.

**Keywords:** Cellulose Fibres (A), wood (A), coupling agents (A), interface (B)

## Introduction

The use of additives in plastics is likely to grow with the introduction of improved compounding technology and new coupling agents that permit the use of high filler content. Over the past decade there has been a growing interest in the use of lignocellulosic fibres as reinforcing elements in polymeric matrices [1,2]. A number of researchers have been involved in investigating the exploitation of cellulose fibres as load bearing constituents in composite materials. Some specific and well known properties of this natural product motivate their association with organic polymers to elaborate composite materials.

However, despite their attractive properties, lignocellulosic fibres are used only to a limited extent in industrial practice due to the difficulties associated with surface interactions. The primary drawback of agro-based fibres is associated with their inherent polar and hydrophilic nature and the non-polar characteristics of most of thermoplastics. It results in difficulties in compounding the filler and the matrix, and therefore in achieving acceptable dispersion levels, which yields composites with low performances. This hydrogen bonding phenomenon is best exemplified in paper where these secondary interactions provide the basis of its mechanical strength. It also results in high moisture absorption and swelling of the fibres. Poor fibre-matrix interface induces a decrease in mechanical properties.

Moreover, the processing temperature of composites is restricted to about 200°C, because of the possible degradation and/or the emissions of volatile compounds that could affect composite properties. Higher temperatures could be used, if the processing time is short. This limits the type of thermoplastics that can be used with polysaccharide fillers to commodity plastics such as polyethylene, polypropylene, poly-vinyl chloride, and

polystyrene. However, it is worth noting that these cheap plastics constitute about 70% of the total thermoplastic-based products consumed by the plastics industry.

Several strategies have been suggested in the literature describing the way to improve the compatibility of lignocellulosic fibres with thermoplastic polymers, e.g.: physical treatment such as surface oxidation activation [3] and chemical modification such as graft copolymerisation [1,4].

In a previous work, the surface chemical modification of microcrystalline cellulose and cellulose fibres obtained from different sugar cane bagasse pulping processes were studied in heterogeneous conditions using modest amounts of octadecanoyl and dodecanoyl chloride [5]. The cooking processes tested were Kraft, organosolv ethanol/water and organosolv/supercritical carbon dioxide. The ensuing surfaces acquired a non-polar character, suitable for incorporating the obtained fibres as reinforcing elements in composite materials based on polymeric matrices. In the present work, we completed the characterisation of the unmodified organosolv/methanol-supercritical carbon dioxide cellulose (SMC) before and after modification with octadecanoyl chloride (SMC-OC) and dodecanoyl chloride (SMC-DC) acids. The resulting materials were analyzed by X-ray photoelectron spectrometry (XPS) and their degree of polymerisation (DP) and zero tensile strength were determined. In addition, both unmodified and modified cellulose fibres have been used to prepare low-density polyethylene/cellulose fibre composites. The prepared composites were characterized in terms of morphology, mechanical behaviour in both the linear and non linear range, and water uptake.

## **Materials and Methods**

**Cellulose fibres:** The fibres used in this work were obtained from organosolv/supercritical carbon dioxide pulping of sugar cane bagasse. The obtained pulp was submitted to a bleaching treatment before modification. This operation involved two stages, viz. stage D (chlorine dioxide) and stage E (alkaline extraction with sodium hydroxide), according to commonly used experimental conditions [6].

**Organosolv/supercritical carbon dioxide pulping:** The experiments were performed in a flow-through supercritical extraction equipment model SFT-250 from Supercritical Fluid Technologies Inc. Sugar cane bagasse was submitted to pulping reactions in a 100 mL stainless steel reactor using 50 mL of methanol/water mixtures as co-solvent and 10g of sugar cane bagasse according to the optimized procedure described by Pasquini *et al.* [7,8]. In this work the experiments were carried out at a temperature of 150°C, a pressure of 23 MPa, for 45 min and with 60% methanol in the methanol/water mixture.

**Chemical modification of the cellulose fibres:** The reactions were carried out under reflux during 4 hours using 2g of cellulose, 100mL of toluene, 0.44mL of dodecanoyl chloride and 0.5mL of pyridine (or 0.57g octadecanoyl chloride and 0.6mL pyridine). At the end of the reaction, the solution was filtered and the modified cellulose fibres submitted to a soxhlet extraction with acetone for two days before drying at 40°C [5]. The reaction scheme is shown in Scheme 1. Scheme 2 gives a schematic illustration aiming at understanding the choice of such treatment. Thus, after the chemical grating of cellulose fibre surface's it becomes much more compatible with non-polar matrices, like polyethylene. As a consequence the quality of the reinforcing elements/matrix interface should be improved

**Cellulose fibres analysis:** The unmodified organosolv/methanol-supercritical carbon dioxide cellulose (SMC) sample, and modified samples with both octadecanoyl chloride (SMC-OC) and dodecanoyl chloride (SMC-DC), were analyzed by (i) X-ray photoelectron spectroscopy (XPS), (ii) determination of the degree of polymerisation (DP) and (iii) measuring their zero tensile strength.

**X-ray Photoelectron Spectrometry (XPS):**

XPS analyses were carried out with the SMC, SMC-DC and SMC-OC samples. For SMC sample the XPS analyses were carried out with the fibres obtained immediately before the bleaching process (SMC-unextracted) and for the same fibres submitted to extraction with toluene for 4 hours and acetone for two days (SMC-extracted). This process was carried out to evaluate the influence of the presence of extractible molecules on the surface of fibres that can be removed during the fibre modification processes. X-ray photoelectron spectra were obtained with a Vacuum Generator ESCALAB 3 MK II instrument, using monochromated MgK $\alpha$  radiation. The measured XPS spectra were not smoothed prior to deconvolution. Peak fitting was carried out for high resolution C1 signals according to Shirley-type background subtraction [9] using curve fitting SURFSOFT programs with the Gaussian-Lorentzian ratio of 60%/40%. Because of possible degradation of cellulose upon prolonged X-rays exposure [10,11], irradiation was kept to a minimum in the present work.

**Measurement of the degree of polymerisation:** The DP of cellulose fibres was determined using the equation 1:

$$\log DP = \frac{(\log 0.75x[\eta])}{0.905} \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity determined according to Standard Test Method TAPPI T230 om-89. This method consists of determining the viscosity of 0.5% cellulose solutions, using 0.5 M cupriethylene diamine as a solvent and a capillary viscosimeter.

**Measurement of zero tensile strength:** The intrinsic strength of the fibres was determined according to Standard Test Method TAPPI T231 cm-85, using tensile instrument from PULMAC TS-100. This method is used to determine an index of the average ultimate strength of longitudinal structure of individual fibres. In the conventional tensile testing machine the jaws are designed such a way that they clamp adjacent area of the tested specimen with practically no jaw separation (zero span) at the beginning of the test. To test the untreated and treaded fibres, 10 pellets of each sample were prepared by pressing the fibres to form film-like material. The average thickness of these films was about 400 microns. The samples were conditioned at 23°C and 50% of relative humidity for 24h.

**Composite Processing:** A HAAKE Rheomix 600 model was used to mix and compound cellulose fibres before (SMC) and after modifications (SMC-OC, SMC-DC) with the polymeric matrix (LDPE pellets). Compounds were prepared by mixing LDPE pellets with cellulose fibres which content ranged between 0 and 30 wt%. The HAAKE Rheomix chamber was filled with this mixture, which was left to melt at 150°C for 10 min using a rotor speed of 60 rpm. After mixing, compounds were hot-pressed at 150°C, in order to assess mechanical properties.

**Composites characterisation:** The composite materials were characterised using (i) Scanning Electron Microscopy (SEM), (ii) Differential Scanning Calorimetry (DSC), (iii) Dynamic Mechanical Analysis (DMA), (iv) Tensile tests and (v) Water absorption.



**Scanning Electron Microscopy (SEM):** SEM was performed with a JEOL JSM-6100 microscope. The specimens were frozen under liquid nitrogen, fractured, mounted and coated with gold/palladium. SEM micrographs were obtained from the fractured region.

**Differential Scanning Calorimetry (DSC):** DSC experiments were carried out with a TA Instrument DSC Q100 using *ca.* 4 mg of the studied material in sealed aluminium capsules. The samples were analyzed by heating-cooling cycles between  $-150$  and  $170^{\circ}\text{C}$ , at a rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ . Measurements were carried out under a nitrogen flow ( $20\text{mL}\cdot\text{min}^{-1}$ ). An empty pan was used as a reference. The melting temperature ( $T_m$ ) was taken as the peak temperature of the melting endotherm, while the heat of melting ( $\Delta H_m$ ) was calculated from the area of the peaks. The degree of crystallinity ( $X_c$ ) calculated from DSC thermograms was determined using the relationship:

$$X_c = \left( \frac{\Delta H_m}{\Delta H_m^o} \right) \left( \frac{100}{w} \right) \quad (2)$$

Where  $\Delta H_m^o = 285 \text{ J}\cdot\text{g}^{-1}$  [12] was taken for 100% crystalline PE matrix and  $w$  is the weight fraction of the matrix material in the composite.

**Dynamic Mechanical Analysis:** DMA measurements were carried out with an apparatus DMA RSA3 from TA Instruments working in the tensile mode. The specimen was a thin rectangular strip with dimensions around  $40 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ . Tests were performed under isochronal conditions at  $1 \text{ Hz}$  and the temperature was varied between  $-120$  and  $120^{\circ}\text{C}$  by steps of  $2^{\circ}\text{C}$ .

**Tensile Tests:** The tensile tests were performed with an Instron 4501 Universal Test Instrument, equipped with a load cell of  $500 \text{ N}$ . The specimens were thin rectangular strips with dimensions around  $40 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ . They were tested using a crosshead speed

of 10 mm min<sup>-1</sup> at 25°C. At least five specimens were tested for each set of samples and the mean values were calculated.

**Water Uptake:** The samples' dimensions for water absorption experiments were 40 mm x 20 mm x 1 mm and were assumed to be thin enough to consider a one-dimensional molecular diffusion. A minimum of three samples was tested for each material. After drying overnight at 105°C, the samples were cooled and weighted, and then immersed into distilled water at room temperature and a pH of 6. The samples were then removed at specific time intervals, blotted to remove the excess of water on the surface and immediately weighted. The water absorption or water uptake (*WU*) was calculated as:

$$WU(\%) = \frac{(M_t - M_0)}{M_0} \times 100 \quad (3)$$

Where:  $M_0$  and  $M_t$  are the sample weights before and after  $t$  min immersion into water, respectively. The mean moisture uptake of each sample was calculated for various conditioning times ( $t$ ) up to equilibrium (stabilisation of the sample weight). The mass of water absorbed at time  $t$ , ( $M_t - M_0$ ), can be expressed as [13]:

$$\frac{M_t - M_0}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right] \quad (4)$$

Where:  $M_\infty$  is the mass adsorbed at equilibrium,  $2L$  the thickness of the polymeric film and  $D$  the diffusion coefficient. For short times, Equation (4) can be written as [14]:

$$\frac{M_t - M_0}{M_\infty} = \frac{2}{L} \left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \quad (5)$$

## Results and Discussion

Figure 1 shows the XPS spectra for unmodified and modified cellulose fibres. All the XPS data for cellulose fibres before and after surface chemical modification are collected in

Table 1. The intensity of the peaks changed substantially for SMC before and after extraction, and the most important modification can be observed for the C1 peak. These changes result from the solvent extraction process, which removes some physically adsorbed molecules from fibres surface. The C1 peak (C-H) corresponds to alkane-type carbon atoms (without any linkage to oxygen atoms) and originates from impurities like extractive substances and fatty acids. The C2 peak (C-O) corresponds to alcohols and ethers, the C3 peak (O-C-O and/or C=O) represents acetal moieties; and the C4 peak (O-C=O) is associated with the presence of carbon atoms in carboxyl groups [10, 11, 15-17]. From Table 1 it can also be verified that the intensity of the C1 and C4 peaks increases and the intensity of the C2 and C3 peaks decreases for SMC-DC and SMC-OC samples with respect to SMC-extracted sample. These changes are modest, but are the consequence of the superficial chemical modification of these samples.

It was already shown by Pasquini et al. [5] that SEM analyses revealed a slight modification carried out with moderate amounts of modifiers (SMC-DC and SMC-OC) preserved the original fibre morphology (SMC). However, the degree of polymerisation (DP) of these fibres was characterised, as shown in Table 2. It can be seen that the surface chemical modification process induces a significant decrease in the DP values. This drastic decrease was probably due to the acidic media in which the modifications were carried out. The reduction of the DP of cellulose is expected to influence the mechanical properties of the fibres and consequently the performance of the resulting cellulose fibres based composites. Thus, the zero tensile strength of the fibres decreased from 1.62 kN for virgin fibres (SMC) to 0.90 and 0.69 kN for SMC-DC and SMC-OC, respectively. It is worth noting that the decrease of the intrinsic strength of cellulose fibres follows the same trend

as that observed for DPs. These data were the average of six measurements and the values obtained are  $\pm 3\%$ .

SEM micrographs of the fractured surface for the composite samples are shown in Figure 2. It corresponds to the surface of fractured LDPE-based composite reinforced with 30 wt% of unmodified cellulose fibres (SMC, panel a), SMC-DC grafted cellulose (panel b) and SMC-OC modified fibres (panel c). The unmodified fibres (SMC composite) are pulled out practically intact from the matrix (Figure 2a), i.e. the fracture of the sample did not lead to the cellulose fibres break. This observation clearly indicates that the interfacial adhesion between the cellulose fibres and the matrix was very poor. The presence of fibre aggregates provides an evidence of the poor dispersion of the filler within the polymeric matrix. On the other hand, the SEM micrographs of modified fibres (Figure 2b and 2c) seem to provide evidence of good cellulose dispersion within the matrix without fibres aggregate formation, and strong interfacial adhesion provided by the cellulose fibres breaking during fracture. This behaviour is a consequence of the surface chemical modification that confers a non-polar character to the cellulose fibres surface, as demonstrated by contact angle measurements [5].

DSC measurements were performed to characterise the thermal behaviour of cellulose fibres filled LDPE films. For each specimen an endothermic peak was observed during the temperature scan. It was obviously ascribed to the melting of crystalline domains of the polymeric matrix. The thermal characteristics ( $T_m$ ,  $\Delta H_m$  and  $X_c$ ) determined or calculated from DSC scans are summarized in Table 3. The degree of crystallinity of the samples was calculated using Equation (2) and then accounted for the effective matrix amount in the composites.  $T_m$  is directly linked to the size of the crystalline domains of LDPE, which can

be influenced by the presence of the filler. For LDPE-based composites, the  $T_m$  is unaffected by the presence of both unmodified (SMC) and modified (SMC-DC and SMC-OC) cellulose fibres, regardless its content and the surface chemical modification to which the cellulose fibres were submitted. This is an indication that the size of the crystalline domains is retained in the matrix. On the contrary, both  $\Delta H_m$  and  $X_c$  were affected by the presence of the filler. For all systems,  $\Delta H_m$  decreases monotonously as the filler content in the composite increases, as expected because of the decrease of the matrix material. Although  $\Delta H_m$  values decreased, the  $X_c$  values increased up to a filler content of 15 w/w and then decreased for higher filler concentration.

These results show that for intermediate filler content, the cellulose fibres seem to act as a nucleating agent for LDPE. However, this effect remains weak because the variation of  $X_c$  values is low. For higher cellulose content, the filler seems to hinder the formation of crystalline domains. Conflicting results are reported in the literature concerning the effect of lignocellulosic fillers on the crystallization of polymeric matrices [18-23]. It seems that the surface chemistry and in particular the lignin content of fibres play an important role in the ability of the filler to promote or hinder the crystallization of the surrounding polymeric matrix.

Dynamic mechanical measurements have been performed for unfilled LDPE and related composite materials filled with 30 wt% of either unmodified (SMC) or modified (SMC-DC, SMC-OC) cellulose fibres. The curve of dependence of the storage tensile modulus ( $E'$ ) vs. temperature at 1 Hz is displayed in Figure 3. The data obtained for the unfilled LDPE matrix were added as reference. The latter is typical of semicrystalline thermoplastic behaviour. At room temperature, the amorphous domains of LDPE are in the rubbery state.

The high storage modulus values reported are ascribed to the reinforcing and physical cross-linking effects of the crystalline regions in the rubbery state. It is observed that the storage modulus decreases slightly when increasing temperature due to the progressive melting of LDPE. After complete melting of crystalline domains (*ca.* 110°C), the elastic tensile modulus drops sharply and irreversibly. This value agrees with melting temperature measured from DSC analysis.

When filled with cellulose fibres, the rubbery modulus of LDPE increases (Figure 3). For instance the storage modulus at 70°C is around  $4.0 \times 10^7$ ,  $1.8 \times 10^8$ ,  $1.2 \times 10^8$ , and  $1.0 \times 10^8$  Pa for the neat LDPE matrix, and composite filled with 30 wt% SMC, SMC-DC and SMC-OC cellulose fibres, respectively. Because the degree of crystallinity of composites was found to remain constant or slightly increased upon filler addition (Table 3), the increase in the rubbery storage modulus for composites should be ascribed to a reinforcing effect of the cellulose fibres. Surprisingly, this effect is higher for unmodified (SMC) cellulose fibres-composites than that associated to modified (SMC-DC, SMC-OC) fibres-based counterparts. This behaviour was unexpected and it could be ascribed to the degradation of cellulose molecules during surface modification process as observed from DP measurements (Table 2) and from the zero tensile strength values. The cellulose degradation and the corresponding decrease of the aspect ratio of the fibres leads to the reduction of the mechanical properties of the cellulose fibres and consequently to the reduction in the rubbery storage modulus. Then, the expected beneficial effect of the increase of adhesion between the surface of the modified fibres and LDPE matrix is counterbalanced by the degradation of the cellulose fibres.

The effect of filler loading on the large strain behaviour of cellulose fibres/LDPE composites was investigated up to the break. The tensile or Young's modulus was determined from the slope of the stress-strain curves in the vicinity of  $\sigma = \varepsilon = 0$ , i.e. for  $\varepsilon < 1\%$ . Results are reported in Figure 4a, which shows the evolution of the tensile modulus versus cellulose fibres content. For all LDPE cellulose fibres filled systems (SMC, SMC-DC and SMC-OC), the evolution of the Young's modulus as a function of filler exhibited a general tendency to increase. The observed increase showed no differences among the different cellulose fibres/LDPE composite samples studied (SMC; SMC-DC and SMC-OC). This result agrees with DMA results, which displayed no discrimination between the various fibres at room temperature.

Figure 4b shows the evolution of the tensile strength as a function of cellulose fibres content. The addition of unmodified SMC cellulose fibres in the LDPE matrix promotes the most considerable reduction in the tensile strength. For SMC-DC and SMC-OC cellulose fibres-based composites the reduction in the tensile strength is less pronounced. This behaviour suggests that the interfacial adhesion between the matrix and the filler is higher for modified fibres, and that the level of dispersion of the filler within the polymeric matrix is also improved. For SMC-DC and SMC-OC samples, the good dispersion and the better interfacial adhesion with the matrix agree with SEM morphological observations.

Figure 4c shows the evolution of the elongation at break *versus* the filler content. The filler causes a dramatic decrease in the elongation at break, even when it is present in very low amount. This well-known decrease in elongation at break upon addition of rigid fillers arises from the fact that the actual elongation experienced by the polymeric matrix is much higher than that measured for the specimen. For the composites filled with 5 w/w cellulose

fibres, it seems that the chemical modification of the filler (either SMC-DC or SMC-OC) results in a higher elongation at break compared to the unmodified fibres-based composite.

The absorption of water for the different composite specimens immersed in water was evaluated as a function of time. The results are shown in Figure 5. Some general remarks can be made: (i) all the composites absorb water during the experiment, but following different behaviours; (ii) the existence of two well-separated regions is reported. At the beginning, the kinetics of absorption is fast, and within the time, it leads to a plateau which value corresponds to the water absorption at equilibrium. The diffusion coefficient ( $D$ ) of water in the different composites was estimated using Equation 5 and by processing the data obtained at short absorption times and the maximum water absorption at equilibrium (99 days). The diffusion coefficient of water ( $D$ ) and water uptake at equilibrium ( $WU$ ) values are collected in Table 4. Both the water uptake and the diffusion coefficient increased when increasing the cellulose fibres content. Except for poorly filled samples (5% w/w), it is observed that the water uptake is much higher for unmodified (SMC) cellulose fibres-based materials compared to that of modified ones (either SMC-DC or SMC-OC cellulose fibres-based composites). Discrimination between the two chemical treatments towards the water sensitivity is also noted. The water uptake is higher for SMC-DC-fibres- compared to SMC-OC fibres- based composites. It is clearly evidenced for 30% w/w filled materials. These observations agree with contact angle measurements performed in our previous study [5]. It was shown that unmodified cellulose displayed a typical high water affinity associated with a fast decrease of the initially low contact angle. For modified samples, an increase of the hydrophobic character of the material was observed. This effect was higher for the acid chloride having the longest aliphatic chain.



## Conclusions

Composite materials were obtained by compounding and moulding cellulose fibres from sugar cane bagasse obtained from organosolv/supercritical carbon dioxide pulping process with low density polyethylene. Lignocellulosic fibres were also used after chemical modification with octadecanoyl and dodecanoyl chloride. The evidence of occurrence of the chemical modification was checked by X-ray photoelectron spectrometry (XPS) and the degree of polymerisation and the zero tensile strength of the fibres were determined. The morphology of ensuing composite materials was characterised by scanning electron microscopy (SEM). The surface chemical modification of cellulose fibres resulted in improved interfacial adhesion with the matrix and higher dispersion level. It also resulted in a better water resistance. However, despite improved compatibility between the filler and the matrix modified fibres-based composites did not show improved mechanical performances when compared to unmodified fibres. This surprising result was ascribed to the strong degradation (as confirmed by the lowering of the DP and the zero tensile strength) of cellulose after chemical treatment despite the mild conditions used. This work in another piece of conviction aiming at demonstrating the need of using renewable materials and showing the necessity of multiplying our efforts to overcome the limitations associated with biomass based-products.

## Acknowledgement

We thank CAPES (Brazil) and COFECUB for financial support.

## References

- [1] Bledzki AK, Gassan J. Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.* 1999;24(2):221-274.

- [2] Eichhorn SJ, Baillie CA, Zafeiropoulos N, Mwaikambo LY, Ansell MP, Dufresne A, Entwistle KM, Herrera-Franco PJ, Escamilla GC, Groom L, Hugues M, Hill C, Rials TG, Wild PM. Review : current international research into cellulosic fibres and composites. *J. Mat. Sci.* 2001;36(9):2107-2131.
- [3] Belgacem MN, Gandini A. The surface modification of cellulose fibres for use as reinforcing elements in composite materials. *Compos. Interfaces* 2005;12(1-2):41-75.
- [4] Freire CSR, Silvestre AJD, Neto CP, Belgacem MN, Gandini A. Controlled heterogeneous modification of cellulose fibres with fatty acids: Effect of reaction conditions on the extent of esterification and fibre properties. *J. Appl. Polym. Sci.* 2006;100(2):1093-1102.
- [5] Pasquini D, Belgacem MN, Gandini A, Curvelo AAS. Surface esterification of cellulose fibres: Characterisation by DRIFT and contact angle measurements. *J. Coll. Interface Sci.* 2006;295(1):79-83.
- [6] Gullichsen J, Fogelholm CJ. *Papermaking Science and Technology*; vol..6, Tappi Press, Atlanta, GA, 1999.
- [7] Pasquini D, Pimenta MTB, Ferreira LH, Curvelo AAS. Sugar cane bagasse pulping using supercritical CO<sub>2</sub> associated with co-solvent 1-butanol/water. *J. Supercritical Fluids* 2005;34(2):125-131.
- [8] Pasquini D, Pimenta MTB, Ferreira LH, Curvelo AAS. Extraction of lignin from sugar cane bagasse and Pinus taeda wood chips using ethanol–water mixtures and carbon dioxide at high pressures . *J. Supercritical Fluids* 2005;36(1):31-39.
- [9] Shirley DA. High-resolution x-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B: Solid State* 1972;B5(12):4709-4714.

- [10] Sapiuha S, Verreault M, Klemberg-Sapiuha JE, Sacher E, Wertheimer MR. X-ray photoelectron study of the plasma fluorination of lignocellulose. *Appl. Surf. Sci.* 1990;44(2):165-169.
- [11] Ahmed A, Adnot A, Grandmaison JL, Kaliaguine S, Doucet J. ESCA analysis of cellulosic materials. *Cell. Chem. Technol.* 1987;21(5):483-492.
- [12] Bryan Ellis. *Polymers – a property database*. Boca Raton (FL): CRC Press, 2000.
- [13] Comyn J. *Polymer Permeability*. J.Comyn, editor. Elsevier Applied Science, New York, 1985.
- [14] Vergnaud JM. *Liquid Transport Process in Polymeric Materials: Modeling and Industrial Applications*. Prentice-Hall, Englewood Cliffs, NJ, 1991.
- [15] Dorris GM, Gray DG. The surface analysis of paper and wood fibres by ESCA (electron spectroscopy for chemical analysis). I. Application to cellulose and lignin. *Cell. Chem. Technol.* 1978;12(1):9-23.
- [16] Gray DG. The surface analysis of paper and wood fibres by ESCA. III. Interpretation of carbon (1s) peak shape. *Cell. Chem. Technol.* 1978;12(6):735-743.
- [17] Belgacem MN, Czeremuskin G, Sapiuha S., Gandini A. Surface characterisation of cellulose fibres by XPS and inverse gas chromatography. *Cellulose* 1995;2(3):145-157.
- [18] Gatenholm P, Kubat J, Mathiasson A. Biodegradable natural composites. I. Processing and properties. *J. Appl. Polym. Sci.* 1992;45(9):1667-1677.
- [19] Luo S, Netravali AN. Mechanical and thermal properties of environment-friendly “green” composites made from pineapple leaf fibres and poly(hydroxybutyrate-co-valerate) resin. *Polym. Compos.* 1999;20(3):367-378.

- [20] Reinsch VE, Kelley SS. Crystallization of poly(hydroxybutyrate-co-hydroxyvalerate) in wood fibre-reinforced composites. *J. Appl. Polym. Sci.* 1997;64(9):1785-1796.
- [21] Dufresne A, Dupeyre D, Paillet M. Lignocellulosic flour reinforced poly(hydroxybutyrate-co-valerate) composites. *J. Appl. Polym. Sci.* 2002;87(8):1302-1315.
- [22] Malainine ME, Mahrouz M, Dufresne A. Lignocellulosic flour from cladodes of *Opuntia ficus-indica* reinforced polypropylene composites. *Macromol. Mater. Eng.* 2004;289(10):855-863.
- [23] Faria H, Cordeiro N, Belgacem MN, Dufresne A. Dwarf cavendish as a source of natural fibres in Polypropylene-based composites. *Macromol. Mater. Eng.* 2006;291(1):6-26.

#### Figure Captions:

**Figure 1.** XPS spectra for cellulose fibres before surface chemical modification (A) SMC-unextracted and (B) SMC-extracted, and after surface chemical modification (C) SMC-DC and (D) SMC-OC.

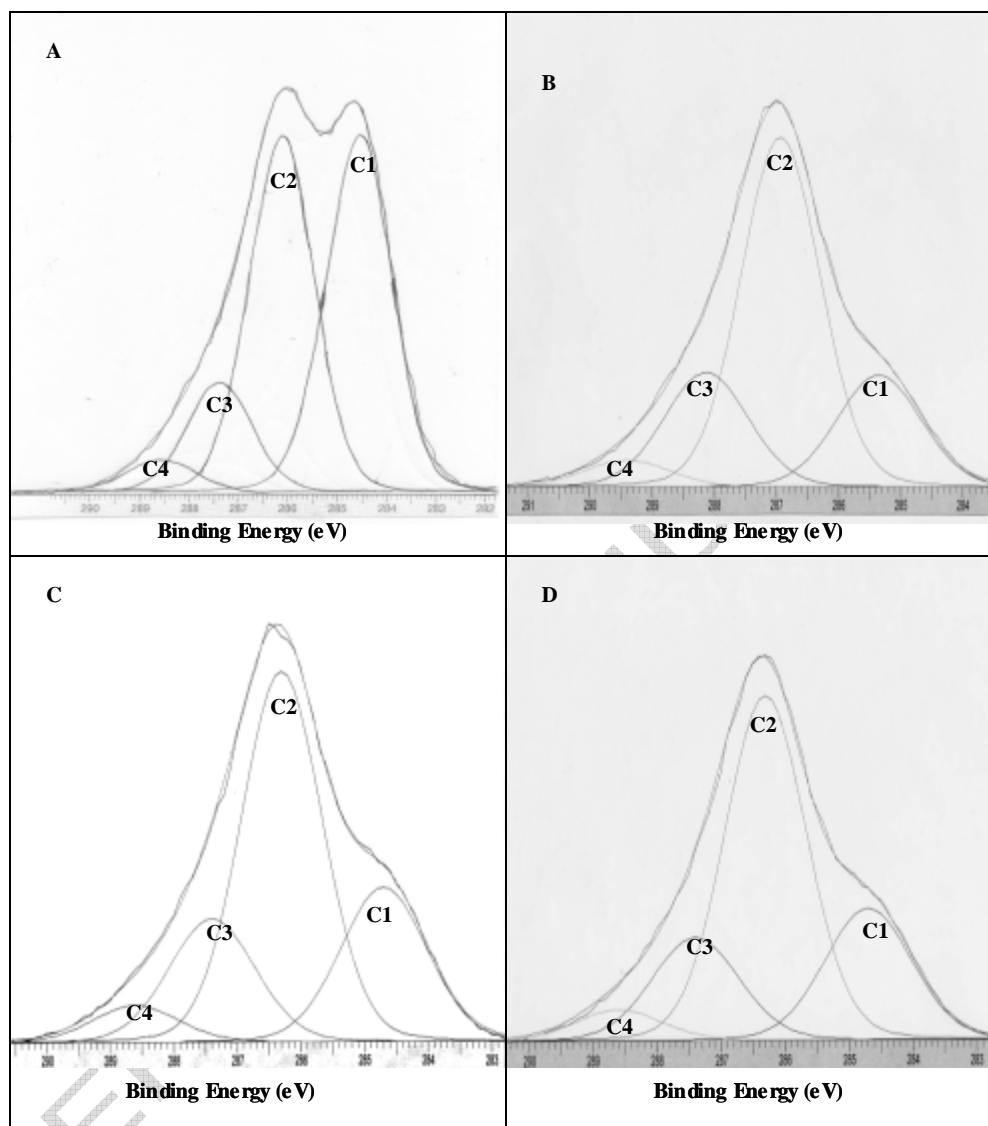
**Figure 2.** Scanning electron micrographs of fractured surface of cellulose fibres/LDPE composites: (A) 30 wt% of SMC fibres, (B) 30 wt% of SMC-DC fibres and (C) 30 wt% of SMC-OC fibres.

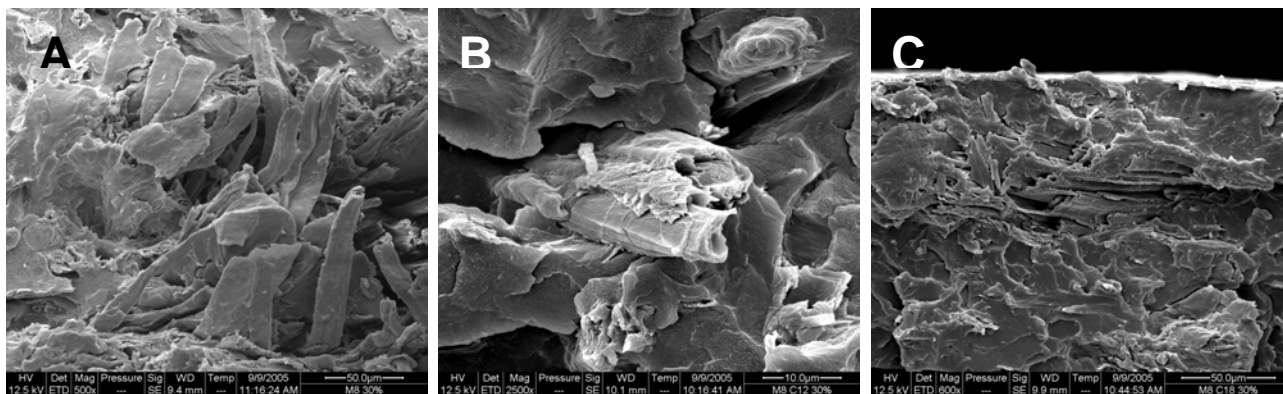
**Figure 3.** Logarithm of the storage tensile modulus  $E'$  vs. temperature at 1Hz for cellulose fibres/LDPE composites: unfilled LDPE matrix ( $\square$ ), and LDPE filled with 30 wt% of SMC ( $\bullet$ ), 30 wt% of SMC-DC ( $\Delta$ ), and 30 wt% of SMC-OC ( $\blacktriangledown$ ) fibres.

**Figure 4.** (a) Young's modulus, (b) tensile strength, and (c) elongation at break of unmodified SMC (●), modified SMC-DC (■), and SMC-OC (▲) cellulose fibres filled LDPE composites versus filler loading.

**Figure 5.** Water uptake versus time for LDPE-based composites when immersed in water at room temperature: unfilled LDPE matrix (■), and LDPE filled with 5 wt% of SMC (●), 5 wt% of SMC-DC (∇), 5 wt% of SMC-OC (□), 15 wt% of SMC (▲), 15 wt% of SMC-DC (○), 15 wt% of SMC-OC (◆), 30 wt% of SMC (▼), 30 wt% of SMC-DC (◇), and 30 wt% of SMC-OC (Δ).

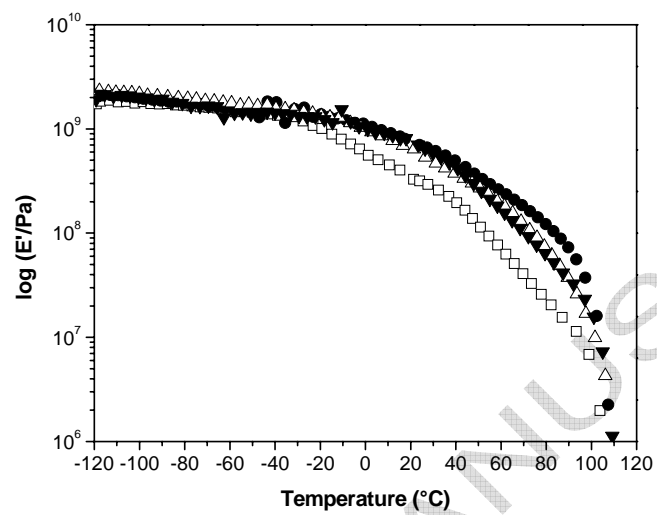
Pasquini et al., Figure 1





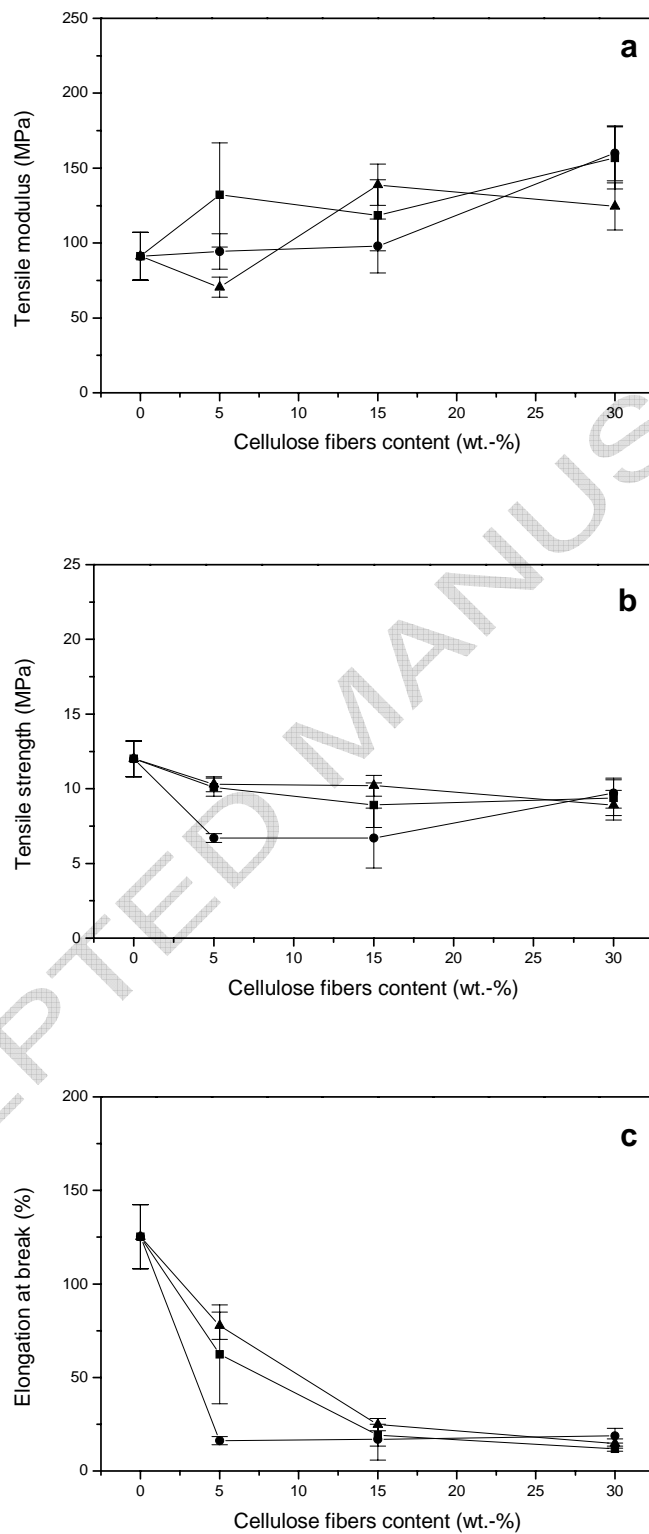
Pasquini et al., Figure 2

Pasquini et al., Figure 3

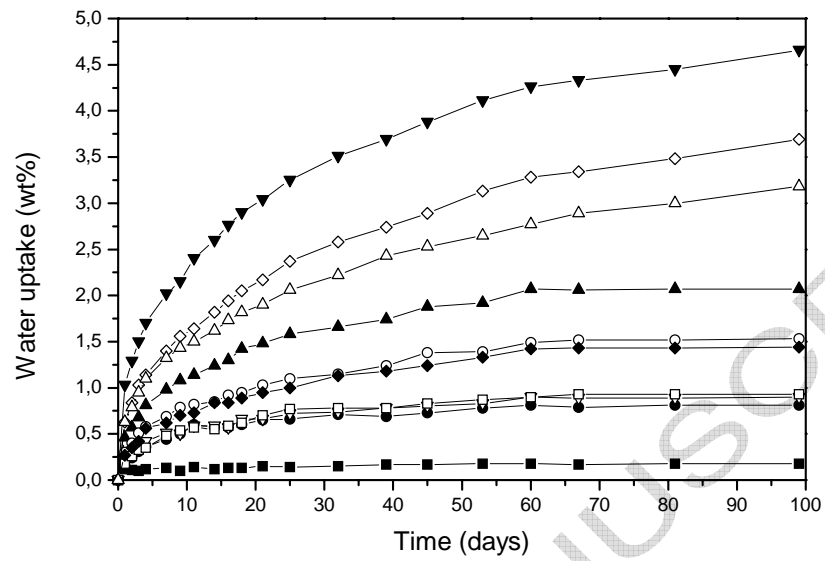




Pasquini et al., Figure 4



Pasquini et al., Figure 5



**Table 1.** XPS analysis of unmodified (SMC), and modified (SMC-DC and SMC-OC) cellulose fibres.

Sample	Binding energy (eV)			
	C1	C2	C3	C4
	CH	CO	OCO	OC=O
	<b>285</b>	<b>286.6</b>	<b>287.8</b>	<b>289.1</b>
SMC-unextracted	41.6	41.4	13.2	3.9
SMC-extracted	19.2	56.5	19.7	4.6
SMC-DC	23.3	52.5	18.6	5.6
SMC-OC	22.3	54.9	17.5	5.3

**Table 2.** Degree of polymerisation (DP) of unmodified (SMC), and modified (SMC-DC and SMC-OC) cellulose fibres.

Sample	DP
SMC	560
SMC-DC	90
SMC-OC	50

**Table 3.** Characteristics of the melting endotherm of cellulose fibres filled LDPE composites using data obtained from DSC curves: melting point ( $T_m$ ), associated heat of fusion ( $\Delta H_m$ ,  $\Delta H_{mc}$ ) and degree of crystallinity ( $X_c$ ) (calculated from  $\Delta H_m$  values and taking into account for the effective matrix content in the composite).

Filler	Fibre content (wt%)	$T_m$ (°C)	$\Delta H_m$ (J.g <sup>-1</sup> )	$\Delta H_{mc}$ (J.g <sup>-1</sup> )*	$X_c$ (%)
LDPE matrix -	0	112	106.0	106.0	37
SMC	5	111	109.6	115.4	41
	15	110	101.4	119.3	42
	30	110	79.0	112.9	40
	5	111	100.6	105.9	37
SMC-DC	15	111	99.5	99.5	41
	30	111	79.1	113	40
	5	112	106.2	111.8	39
SMC-OC	15	111	105.8	124.5	44
	30	109	77.2	110.3	39

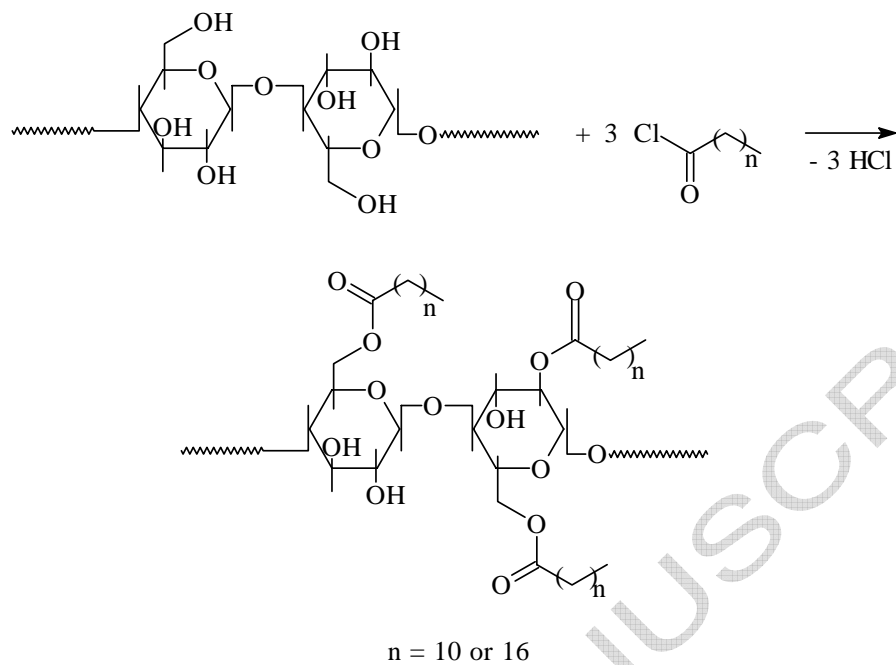
(\*)  $\Delta H_{mc} = \frac{\Delta H_m}{w}$ , where  $w$  is the weight fraction of polymeric matrix material in the composite.

**Table 4.** Water uptake at equilibrium (WU) and diffusion coefficient of water (D) for LDPE based composites when immersed in water at room temperature.

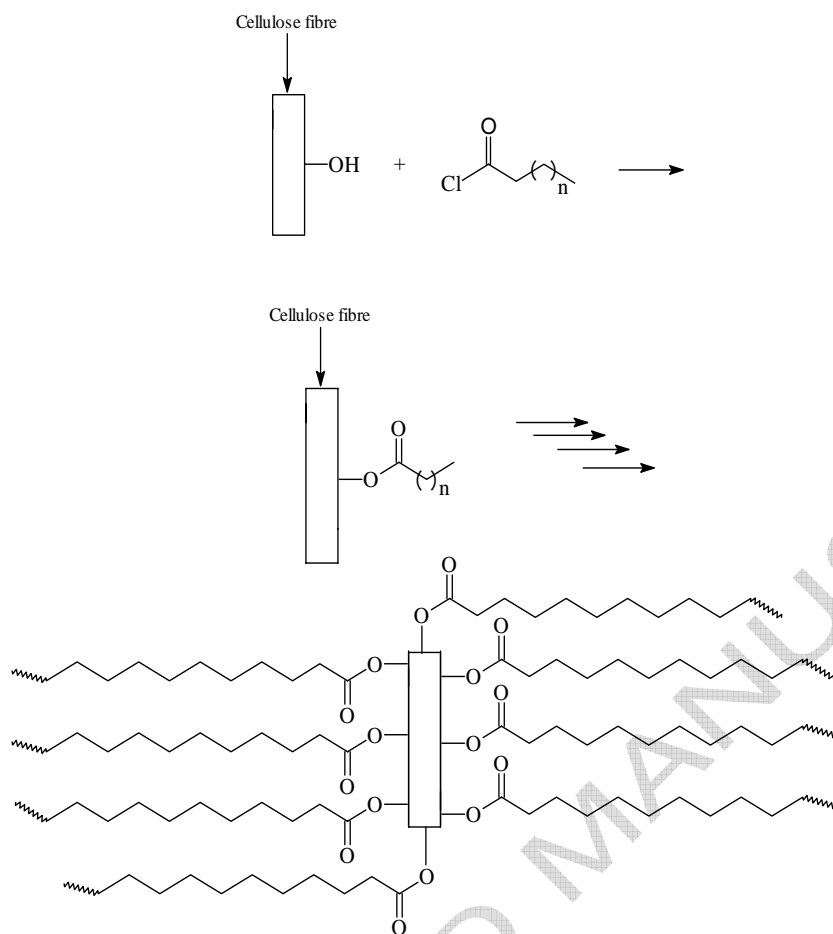
Filler	Fibre content	Water immersion		
		wt%	WU (%)	$D$ (cm <sup>2</sup> .s <sup>-1</sup> x 10 <sup>-13</sup> )
LDPE matrix	-	0	0.18	0.881
SMC	5	5	0.81	0.693
	15	15	2.07	5.46
	30	30	4.66	12.27

<b>SMC-DC</b>	5		1.31
		0.90	
	15		4.08
		1.53	
	30		12.47
<b>SMC-OC</b>		3.69	
	5		1.80
		0.93	
	15		1.77
		1.44	
	30		12.47
		3.18	

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**Scheme 1.** Schematic reaction of modification of cellulose fibre.



**Scheme 2.** Schematic illustration aiming at understanding the choice of the treatment.