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Cellulose-reinforced Composites: From Micro-to Nanoscale

Alain Dufresne* and Mohamed N. Belgacem

Institut Polytechnique de Grenoble (Pagora),
Laboratoire de Génie des Procédés Papetiers (LGP2),
UMR CNRS 5518 Domaine Universitaire, 461, Rue de la Papeterie - BP 65,
F-38402, St Martin d'Hères, France

Authors:

Alain Dufresne
Telephone: + 33 4 7682-6995
Fax:+ 33 4 7682-6933
**E-mail: alain.dufresne@pagora.grenoble-inp.fr*

Mohamed N. Belgacem
Telephone: + 33 4 7682-6962
Fax: + 33 4 7682-6933
E-mail: naceur.belgacem@pagora.grenoble-inp.fr

Abstract: This paper present the most relevant advances in the fields of: i) cellulose fibres surface modification; ii) cellulose fibres-based composite materials; and iii) nanocomposites based on cellulose whiskers or starch platelet-like nanoparticles. The real breakthroughs achieved in the first topic concern the use of solvent-free grafting process (plasma) and the grafting of the matrix at the surface of cellulose fibres through isocyanate-mediated grafting or thanks to "click chemistry". Concerning the second topic, it is worth to mention that for some cellulose/matrix combination and in the presence of adequate aids or specific surface treatment, high performance composite materials could be obtained. Finally, nanocomposites allow using the semi-crystalline nature and hierarchical structure of lignocellulosic fibres and starch granules to more deeply achieve this goal profitably exploited by Mother Nature

Keywords: *Cellulose fibres, surface modification, composite materials, nanocomposites.*

Introduction

The exploitation of cellulose fibres and/or nano-whiskers constitutes a rapidly growing issue, because it fits very well with the marked tendency of using renewable biodegradable raw materials[1,2]. In fact, these reinforcing elements possess mechanical properties similar to those of mineral-based counterparts. Unfortunately, natural organic fibres display two major limitations when used as reinforcing elements in composite materials, namely: i) they have a strong sensitivity to water and moisture; and ii) they display poor compatibility with the hydrophobic polymeric matrices generally used in this field. The consequences of such features are dramatic in composite materials context, because the moisture adsorption induces a loss of their mechanical properties and the poor compatibility yields weak interfacial adhesion and dispersibility, and consequently low performance composites.

Lignocellulosic fibres consist of cellulose microfibrils embedded in a cementing matrix of other, mostly hemicelluloses and lignin, polymers. The properties of natural fibres are strongly influenced by many factors, particularly chemical composition and internal fibre structure, which differ between different parts of a plant as well as between different plants. In most natural fibres the microfibrils orient themselves at an angle to the fibre axis called the "microfibril angle". A weak correlation between strength and cellulose content and microfibril or spiral angle is found for different plant-fibres. In general, fibre strength increases with increasing cellulose content and decreasing spiral angle with respect to fibre axis. This means that the most efficient cellulose fibres are those with high cellulose content and low microfibril angle. Depending on their origin, the microfibril diameters range from about 2 nm to 20 nm for lengths that can reach several tens of microns. As they are devoid of chain folding and contain only a small number of defects, each microfibril can be considered as a string of cellulose monocrystals, linked along the microfibril by amorphous domains, and having a modulus close to theoretical limit for cellulose. The promise behind cellulose-derived composites lies in the fact that the axial Young's modulus of the basic cellulose crystalline nanocrystal derived from theoretical chemistry is potentially stronger than steel and similar to Kevlar.

Cellulose whiskers or nanocrystals are highly crystalline and elongated nanoparticles extracted from lignocellulosic fibres by specific treatments inducing a spectacular enhancement of the mechanical properties of polymeric matrices[3,4].

The last two decades, our research group has developed a wide research activity based on the use of cellulose fibres and whiskers from different origins and morphologies, including the investigation of several modification approaches, the improvement of thermoplastic and thermosetting polymeric matrices and the preparation of a variety of nanocomposites, involving the use of cellulose and chitin-based nanowhiskers, starch-based nanoplatelets. The main aims of the cellulose fibres surface modification strategies are: i) to provide them an efficient hydrophobic barrier; ii) to minimise their interfacial energy with the non-polar polymer matrix, thus generating optimum adhesion and dispersion; and iii) to graft coupling agents bearing the matrix in mind, in order to yield the best interface between the two phases or even to create fibre-matrix covalent bonds. We have developed different modification strategies using experimental condition preserving the fibre integrity in order to take advantage from their reinforcing character[5-7].

The main objective of using nanoscale reinforcing elements is to achieve further improved fibres and composites by eliminating the macroscopic flaws by disintegrating the natural grown fibres, and separating the almost defect-free highly crystalline fibrils. Indeed, a big variation of properties is observed for lignocellulosic fibres, which is inherent to natural products. When changing the dimensions of the reinforcing phase, some important changes occur. The specific area is considerably increased from few $m^2.g^{-1}$ to few 100 $m^2.g^{-1}$. The average inter-particles distance decreases as their size decreases, allowing particle-particle interactions. Improved properties can be reached for low filler content without detrimental effect on properties such as impact resistance and plastic deformation. Finally, a reduction of gas diffusion can be observed (barrier effect).

We have recently reviewed the main achievement associated to the present topic[2,5-7]. We therefore will limit the content of the present paper to the main breakthrough performed within our own investigations during the last three years and we invite the reader to consult our reviews for the older studies. The investigations carried out in our research group dealt with three different but closely linked aspects: i) the development of new grafting strategies; ii) the testing of conventional modification strategies in the field of cellulose based composites; and iii) the preparation of nanocomposites. We therefore suggest reporting the recent advances achieved by our group according to these three sections.

Materials and Characterisation Methods

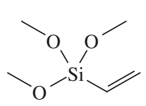
Different cellulosic substrates were used, namely: lignocellulosic fibres from numerous wood and annual plants (bleached, unbleached, mechanically treated, ...), microcrystalline powders (Avicell, technocell, etc.), Whatman filter paper made from high-purity cellulose and laboratory made paper sheets from different substrates.

The main characterisation techniques, traditionally performed to assess the occurrence and the extent of the modification include FTIR and XPS spectroscopy, elemental analysis, contact angle measurements, inverse gas chromatography (IGC), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and scanning electron microscopy (SEM). The characterisation of the composites was performed using Dynamic Mechanical Analysis (DMA), Tensile tests, Differential Scanning Calorimetry (DSC), Thermogravimetric Analyses (TGA) and water or moisture uptake and release. Transmission Electron Microscopy was also used to characterise the nanoparticles prepared from different sources.

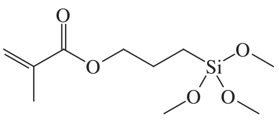
Chemical Modification

Starch nanoparticles were successfully grafted with poly(tetrahydrofuran), poly(caprolactone), and poly(ethylene glycol) monobutyl ether chains using toluene 2,4-diisocyanate as a coupling agent[8]. The surface grafting efficiency was confirmed by Fourier transform infrared and X-ray photoelectron spectroscopy, differential scanning calorimetry, elemental analysis, and contact angle measurements. The grafting density decreased with increasing the length of the polymeric chains. The resulting modified nanoparticles can find applications in the field of co-continuous nanocomposite materials.

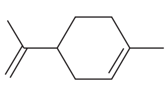
Our group has recently published two papers dealing with the use of plasma treatment of cellulose fibres from bleached hardwood Eucalyptus. Different coupling agents were used to modify these substrates, namely vinyl trimethoxysilane, VTS, γ-methacrylopropyl trimethoxysilane, MPS[9], myrcene, My, limonene, LM[10]. Different experimental parameters were varied, namely: treatment time, plasma power, modification procedure (gas-plasma, activation-impregnation, etc.). After the treatment, modified substrates were extensively solvent extracted in order to remove the physically adsorbed unbound molecular fragments, before being submitted to different characterisation techniques, namely: contact angle measurement and X-ray photoelectron Spectroscopy. Both techniques showed that the chemical grafting has indeed occur, since the contact angle value of a drop of water deposited at the surface increased from about 40° for unmodified substrate to more than 100° for all the treated cellulosic samples. The use of different liquid probes and the processing of the resulting contact angle values following Owens-Wendt approach revealed that the polar component of the surface energy decreased from about 23 mJ/m^2, for pristine samples, to practically zero for all the treated samples, as shown in Figure 1.



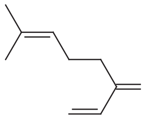
VTS



MPS



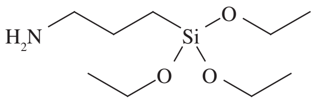
LM



My

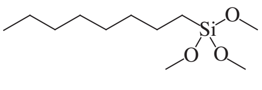
The XPS spectra related to VTS- and MPS-treated samples revealed the appearance of two new peaks at 102 and 150 eV, associated with the presence of Si atoms. The deconvoluted C_{1s} spectra of the treated cellulose displayed a significant the intensity of C1 peak, i.e., from about 17% to around 48, 57, 55 and 92%, for VTS-, MPS-, LM- and My-treated samples, respectively. The obtained data suggested that My has a higher reactivity than LM, which could be expected from its chemical structure (it contains a higher number of double-bound functions). In fact, deconvoluted C_{1s} spectrum of My-treated surface was largely dominated by C1 signal (92% of C-H moieties), indicating that after treatment the surface became mainly composed of aliphatic sequences. When comparing the two silane coupling agents between themselves, MPS was found to be more reactive than VTS.

The reaction between alkoxysilane coupling agents and cellulose has been extensively studied by our group, including the deep investigation of the pre-hydrolysis step, i.e., kinetics of hydrolysis, solvolysis and self-condensation reactions, as a function of temperature and pH, as well as the adsorption isotherms of the pre-hydrolysed species onto the cellulose surface. An extensive review devoted to silane coupling agents within the context of cellulose grafting is under preparation[11]. Thus, various alkoxysilanes were tested in this context, with a special emphasis and deep investigation of the following molecules: γ-aminopropyltriethoxysilane (APS), γ-methacrylopropyltriethoxysilane (MPS) and γ-mercaptopropyltriethoxysilane (MRPS).

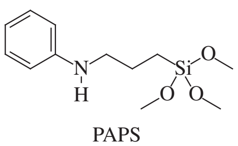


APS

The adsorption of such molecules and their grafting at cellulose surface was recently reported by[12], who used the following alkoxysilanes: MPS, MRPS, octyl trimethoxysilane (OS) and *N*-phenyl-γ-aminopropyl trimethoxysilane (PAPS).



OS



PAPS

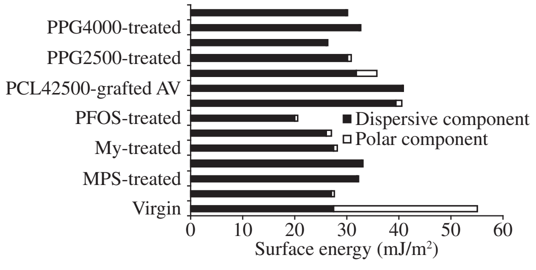


Figure 1. Dispersive and polar components of surface energy of different cellulose surfaces, before and after modification.

This study involved the use of Technocel 150DM, as a model cellulosic substrate and permitted establishing the optimal pre-hydrolysis reaction conditions to achieve the maximum adsorption of pre-hydrolysed species at cellulose surface, for each silane used. After a thermal treatment to induce the grafting, the modified surfaces were characterised by contact angle measurements and XPS, which, both, confirmed the occurrence of the grafting.

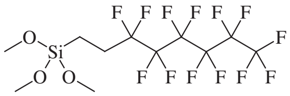
We have recently published three papers with the main idea of attaching the matrix to the surface of cellulose fibres *via* chemical linkage. The thus modified reinforcing elements will therefore bear long chains at their surface which can entangle with those originating from the polymer matrix[13-15]. As a consequence, continuous covalent bonding will join the two components of the composite. In this context, we tested polycaprolactone (PCL), poly(ethylene oxide), poly(propylene oxide) and poly(tetrahydrofuran), due to their thermoformable character and/or biodegradable properties.

The first paper called upon the use of "click-chemistry"[13], using two steps reaction pathways. The first step consisted of reacting undecynoic acid with cellulose yielding a cellulosic substrate bearing multiple C≡C-terminated hairs, whereas the second one involved the condensation between the modified substrate and a previously prepared azido-terminated polycaprolactone (PCL), in heterogeneous conditions, through "click chemistry". All the intermediates as well as the final products were carefully characterised by FTIR, ^{13}C-NMR and XPS spectroscopy and elemental analyses. The XPS has showed clear cut evidences about the grafting occurrence. The weight gain achieved in such conditions reached significant amount, i.e., about 20%[13].

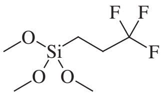
The second paper reported the grafting of cellulose fibres by PCL according to another reaction pathway, i.e., the use of phenyl isocyanate, as an OH-blocking agent and 2,4-toulene diisocyanate (TDI), as a PCL-Cellulose coupling mediator[14]. The polar component of the surface energy of cellulose decreased drastically and vanished to practically zero after grafting, as illustrated by Figure 1. XPS spectroscopy revealed the presence of nitrogen atoms (peak at around 398 eV) at the surface of the modified cellulosic substrate. The intensities of C1 and C4 peaks have also increased significantly after grafting. In fact, the intensity of C1 increased from about 15% up to more than 50%, for the most efficiently modified substrates. The intensity of C4 peak followed the same trend. In addition, the O/C ratios increased from 0.8 to less than 0.3, indicating that the surface was significantly enriched by C atoms. The biodegradable potential of the modified substrates was found to remain unchanged albeit with a slower biodegradation kinetics.

The last paper involved the use of oligoether chains to modify cellulose[16], namely: poly(ethylene-) and poly(propylene-oxides) (PPO) and poly(tetrahydrofuran) (PTHF). The reaction pathway used here is the same applied for PCL-cellulose preparation involving isocyanate mediators. The main results obtained for oligoethers and associated with the grafting efficiency were similar to those obtained for PCL, in terms of wettability, XPS data and biodegradability. Figure 2 represents SEM micrographs of softwood long fibres, before and after PPG treatment.

Avicell (AV), as well as that of Whatman paper (WP) were grafted by two fluorine-bearing alkoxysilane, namely: 3,3,3-trifluoropropyl trimethoxysilane (FPTS) and 1H,1H,2H,2H,perfluorooctyl trimethoxysilane (FOTS)[15]. Here also non-swelling experimental conditions were used, in order to limit the modification to the surface of the substrates tested. The resulting modified fibres were characterized by elemental analysis, contact angle measurement, X-ray photoelectron spectroscopy and Scanning Electron Microscopy (SEM-EDS). All these techniques showed that the grafting has indeed occurred. Thus, the water contact angle deposited at the surface of AV and WP shifted from around 50° before modification to 115° and 125° for FPTS-treated and TFOS-modified samples, respectively. The value of the polar component of surface energy of the modified surfaces has vanished to 0 mJ/m^2, as presented in Figure 1.



FPTS



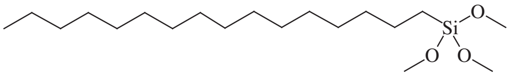
FOTS

The XPS spectra revealed the presence of Si peaks at 102 and 150 eV and F signal at 688 eV for the grafted samples. The first silicon peak is associated to the potoelectrons ejected from Si$_{2s}$ orbitals, whereas the second one is originated from Si$_{2p}$. Moreover, the deconvolution of C1s spectra related to FPTS- and TFOS-grafted cellulose displayed the following changes when compared to that of pristine substrates: i) the appearance of C-Si and CF_3 peaks at 283 and 292 eV, respectively; ii) the detection of a CF_2 signal at 290 eV in the FPTS-grafted substrate; and iii) a significant increase of the C1 signal in all the spectra of modified substrates.

Rapid and efficient approach to the hydrophobization and lipophobization of cellulose fibers by their reaction with gaseous trichloromethylsilane (TCMS) was also developed very recently[17]. The thus modified surface were characterized by FTIR-ATR and solid-state ^{29}Si NMR spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), contact angle measurements with different liquids and energy-dispersive X-ray spectrometry (EDS). In addition, the paper cohesive energy and zero span properties of the fibres constituting the fiber-mat were assessed before and after the treatment. The modification generated an inorganic coating around the fibers, associated with the construction of a three-dimensional network of Si-O-Si bridges partly bound to the polysaccharide macromolecules. As a consequence, high hydrophobicity and lipophobicity to the samples even when the treatments applied modest TCMS quantities and reaction times as short as 30 seconds. Thus, the contact angles of a drop of water at the surface of the modified surfaces reached values as high as 136°. The XPS spectra confirmed the occurrence of the grafting by detecting Si atoms at the surface of the modified substrates (more than 17% for the most efficiently grafted substrates). The C1 signal increased from about 8 to more than 60%.

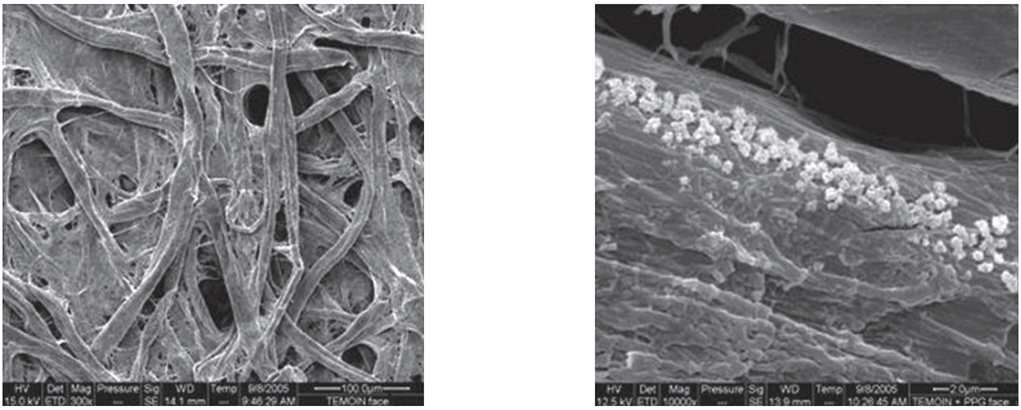
Cellulose-fibres Based Composites

Four different cellulose fibres with different average lengths in combination with two thermoplastic matrices were used to prepare various composite materials. The used fibres were Avicel, technocel, alfa pulps and pine fibres, whereas the matrices involved were low density polyethylene and natural rubber[18]. The prepared cellulose-reinforced composites were characterized, in terms of mechanical performances, thermal properties and water absorbance behaviour. The fibres were used as such and after chemical surface modification with three silane coupling agents, namely MPS, MRPS and hexadecyltrimethoxy-silanes (HDS).



HDS

As expected, the incorporation of the fibres into the matrices increased their mechanical stiffness. Such tendency was more pronounced for composites made of with higher average fibre length. The composite materials prepared using both matrices and cellulose fibres treated



(a) (b)

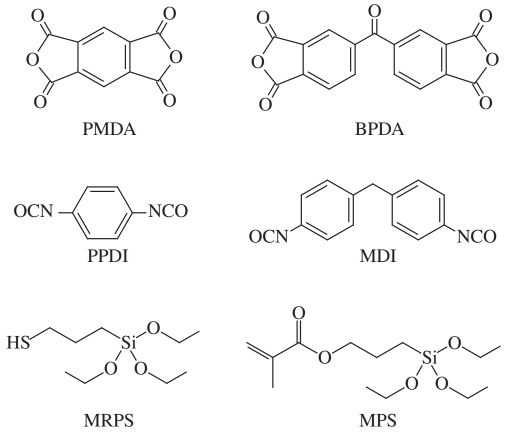
Figure 2. SEM micrographs of Whatman paper (WP) a) before; and b) after PPG-grafting.

with MPS and MRPS displayed good mechanical performances. HDS-treated fibres enhanced the composite properties only modestly, which was attributed to the incapacity of HDS to bring about covalent bonding with the matrix.

Composite materials based on cellulose aceto-butyrate as a matrix and cellulose fibres from softwood long fibres (SLF) and avicell powder as reinforcing elements were prepared[19]. The surface of the reinforcing phase was chemically modified with different coupling agents, namely: two difunctional anhydrides, two diisocyanates, and two alkoxysilanes, namely: pyromellitic dianhydride (PMDA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BPDA), 1,4-phenylene diisocyanate (PPDI), methylene-bis-diphenyl diisocyanate (MDI), and γ-mercaptopropyltriethoxysilane (MRPS), and γ-methacrylopropyltriethoxysilane (MPS). The main idea of such an approach is the use of stiff monomers able to react with the cellulose surface with only one of the functionalities, thus leaving the remaining second moiety to couple with the polymer matrix during composite processing. Such a system gives rise to the formation of a covalent linkage between the matrix and the reinforcing elements and enables perfect stress transfer between the matrix and the reinforcing elements. The stiff character of the used molecules excludes the reaction of both functionalities at the surface of the same fibre whereas their quite small size avoids bridging two fibres.

The modified fibres were submitted to solvent extraction prior characterization by elemental analysis, infrared and X-ray photoelectron spectroscopy, scanning electron microscopy (SEM) and contact angle measurements. All these techniques confirmed the occurrence of the grafting. The modified fibres have kept their biodegradable character, as illustrated by Figure 3.

The modified fibres were then incorporated into cellulose acetate-butyrate and natural rubber matrices. PMDA- and BPDA-treated Avicell were found to reinforce efficiently the mechanical properties of CAB, whereas MPS-treated cellulose enhanced those made with natural rubber matrix.



Pasquini et al.[20] have modified cellulose fibres from sugar cane bagasse with octadecanoyl and dodecanoyl acids chlorides. These fibres were obtained from organosolv/supercritical carbon dioxide pulping process sugar cane bagasse. The occurrence of chemical modification was checked by X-ray photoelectron spectrometry. The modified fibres were then used to reinforce low density polyethylene and showed that the surface chemical modification resulted in improved interfacial adhesion with the matrix and much more homogeneous distribution of the reinforcing elements into the matrix. Even though, the surface modification did not induce an improved mechanical performance of the ensuing composites. This surprising finding was attributed to the fact that the modification procedure affected negatively the degree of polymerisation of the fibres and their intrinsic properties (zero tensile strength). The degradation of these two parameters was associated to the hydrolytic action of acid chloride molecules released during the modification with alcanoyl acids chlorides.

Different Egyptian industrial crops, namely: cotton stalk, rice straw, bagasse, and banana plant waste were used as a starting raw material to produce lignocellulosic fibres, which were incorporated into organic matrices[21]. The matrices used were low density polyethylene and stearic acid as compatibilizer, or maleated low density polyethylene. The properties of the prepared composites were studied by differential scanning calorimetry (DSC), tensile tests and scanning electronic microscopy (SEM). As expected, enhanced mechanical properties were obtained when using maleated LDPE as compatibilizer. The chemical composition of fibres, in terms of lignin, cellulose and hemicelluloses contents, was found to have a strong influence on the mechanical properties of the composites.

Long and short date palm tree fibres were combined with an epoxy matrix to produce composite materials[22]. The long fibres have a length and diameter of around 25 mm and 2 mm, respectively, whereas the short one possessed a length and diameter of around 10 and 0.5 mm, respectively. This study permitted to establish that strong interactions between both components and etherification reactions may occur between the hydroxyl groups of the fibres and the epoxy groups of the epoxy-amine reactive mixture (Figure 4). These effects were emphasized when decreasing the size of the fibres. The higher adhesion between the short fibers and the polymeric matrix, as well as an increased glass transition temperature resulted in a lowered molecular mobility and water absorption level.

Short date palm tree lignocellulosic fibres were incorporated into poly(propylene) and low density

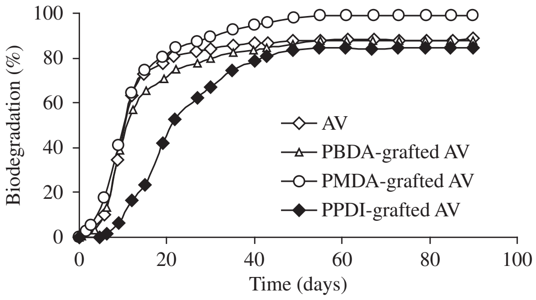


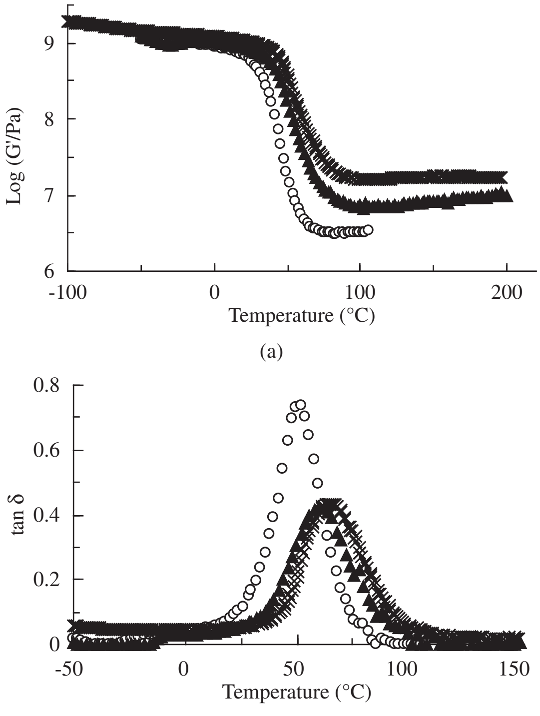
Figure 3. Biodegradation kinetics of Avicell powder, before and after modification with different coupling agents.

polyethylene matrices, in the presence of maleic anhydride copolymers, as compatibilising agent[23]. The properties of the resulting composites were characterized by SEM, DSC and tensile tests. The reinforcing efficiency of the unmodified fibres was found to depend on the nature of the matrix, particularly on their degree of crystallinity. The compatibilization enhanced the mechanical performances for both sets of composites up to a critical amount.

Last year we had the opportunity to test the effect of the fibres modification in cement based composites[24]. Bleached Eucalyptus fibres were grafted by γ-methacryloxypropyltri-methoxysilane (MRPS) and γ-aminopropyltri-ethoxysilane (APS). The surface modification was found to affect the fibre-matrix interface and the mineralization of the fibre lumen, as evidenced by scanning electron microscopy (SEM) with backscattered electron detector. The accelerated ageing cycles showed that MRPS-modified fibres were well protected, since they were free from cement hydration products. Instead, APS-modified homologues underwent rapid mineralization. These observations helped understanding the mechanisms of degradation of fibre-cement composites.

Nanocomposites

Our group has a long tradition in studying nanocomposites based on cellulose, starch or chitin nano-reinforcing elements. Conceptually, nanocomposites refer to multiphase materials where at least one of the constituent phases has one dimension less than 100 nm. This field has attracted the attention, scrutiny and imagination of both scientist and industrial communities in recent years. Behind the push for nanocomposites, a large window of opportunity has opened to overcome the limitations of traditional micrometer-scale composites. Research in this scope is literally exploding because of the intellectual appeal of building blocks on the nanometer scale and because the technical innovations permit to design and create new materials and structures with unprecedented flexibility, improvements in their physical properties and significant industrial impact.



(a)

(b)

Figure 4. a) Logarithm of the storage shear modulus; and b) loss factor tan δ vs. temperature at 1 Hz for epoxy films filled with palm tree fibers: neat polyepoxy matrix (○), and composites reinforced with long (▲) and short palm tree fibers (x).

Stable aqueous suspensions of polysaccharide nanocrystals can be prepared by acid hydrolysis of the biomass[25]. The biomass is generally first submitted to a bleaching treatment with NaOH in order to purify the polysaccharide by removing other constituents. The bleached material is then disintegrated in water, and the resulting suspension is submitted to a hydrolysis treatment with acid. The amorphous regions act as structural defects and are responsible of the transverse cleavage of the microfibrils into short monocrystals under acid hydrolysis. Under controlled conditions, this transformation consists of the disruption of amorphous regions while leaving the monocrystalline segments intact. It is ascribed to the faster hydrolysis kinetics of amorphous domains compared to crystalline ones. The resulting suspension is subsequently diluted with water and washed by successive centrifugations. Dialysis against distilled water is then performed to remove free acid in the dispersion. Complete dispersion of the whiskers is obtained by a sonication step.

The study of cellulosic nanoparticles as a reinforcing phase in nanocomposite films started fifteen years ago[26] and since this time, a huge amount of literature has been devoted to nanocellulose which is becoming a topical subject as revealed from the abundant literature.

Nanocomposites films have been processed from nanoplatelet-like starch particles and plasticized and disrupted starch granules with water and sorbitol[27]. The nanocomposite films were processed by film-casting from a mixture of the aqueous suspension of starch nanocrystals with the gelatinized starch. The thermal and mechanical properties of the nanocomposite films were determined before and after accelerated ageing.

Whiskers from tunicin, the cellulose extracted from tunicate, a sea animal, were used in combination with sorbitol plasticized waxy maize starch to produce nanocomposite materials[28]. The mechanical properties of the prepared materials were studied in the linear and nonlinear deformation domains. The prepared nanocomposites displayed good mechanical strength due to the strong interaction between tunicin whiskers, matrix, plasticizer (sorbitol), and water. In addition, the capacity of the cellulose filler to form a stiff three-dimensional network thanks to hydrogen bonds, contributes to this enhancing power. High loading level induced a decrease in the crystallinity of the amylopectin phase. The mechanical strength increased linearly with filler contents, indicating that an effective stress transfer from the matrix to the whiskers took place. As expected, the mechanical properties of the nanocomposites strongly depended on the relative humidity conditions of the surrounding atmosphere.

Copolymers of polyvinyl alcohol and polyvinyl acetate and a colloidal aqueous suspension of cellulose whiskers prepared from cotton linter were mixed with the aim of preparing nanocomposite materials[29]. The degree of hydrolysis of the matrix was varied in order: i) to vary the hydrophilic-hydrophobic balance the polymer matrix; and ii) to influence the degree of interaction between the filler and the matrix. The prepared nanocomposite films were conditioned at various moisture contents and their dynamic mechanical and thermal properties were established using dynamic mechanical analysis and differential scanning calorimetry, respectively. Tensile tests were also performed at room temperature to estimate mechanical properties of the films in the non linear range. In all cases, fully hydrolysed PVA-based composites displayed stronger filler/matrix interactions when compared with those made with partially hydrolyzed matrix (Figure 5). Conditioning the films in moist conditions revealed that there is a water accumulation at the reinforcing elements-matrix interface. The reinforcing effect was found to increase with increasing the degree of hydrolysis of the matrix.

Nanocrystals from ramie fibres and waxy maize starch granules were grafted by polycaprolactone (PCL) chains with various molecular weights, using isocyanate-mediated reaction[30]. The modified nanoparticles were characterized by X-ray diffraction analysis and contact angle measurements, which showed that the nanoparticles kept their initial morphological integrity and native crystallinity. Then, nanocomposite films were prepared from unmodified and PCL-grafted nanoparticles and PCL as matrix, using casting/evaporation technique. The grafting of PCL chains induced a decrease in the modulus values and an increase in the strain at break.

Chitin whiskers were isolated and polycaprolactone grafted (CHW-g-PCL) in view of preparing thermoformable bionanocomposites[31-34]. The grafting was achieved by initiating the ring-opening polymerization ("grafting from" strategy) of caprolactone monomer onto the CHW surface under microwave radiation. The bionanocomposites prepared were injection-moulded forming a co-continuous phase mediated with the entanglement of grafted PCL chains. The ensuing CHW-g-PCL moulded sheets were characterized by FTIR, XRD, SEM, DSC, DMTA, contact angle measurement, and tensile test. It was established that increasing the PCL content in CHW-g-PCL films, induced an increase of the strength and elongation as well as of the hydrophobicity of the nanocomposites.

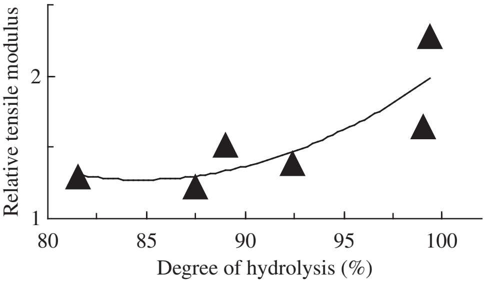


Figure 5. Evolution of the relative tensile modulus of 12 wt.% cotton whiskers reinforced PVA nanocomposite films conditioned at 0% RH as a function of the degree of hydrolysis of the matrix. The solid lines serve to guide the eye.

New nanocomposites of waterborne polyurethane (WPU) as a matrix were prepared by filling low loading of starch nanocrystals (StNs) as a nano-phase[35]. The resulting materials possessed enhanced strength, elongation and Young's modulus. The chemical grafting of the StNs did not affect positively the strength and elongation, because such a treatment inhibited the formation of physical interaction and increasing network density in nanocomposites.

Cellulose rodlike nanocrystals whiskers were surface-grafted with polycaprolactone (PCL) via microwave-assisted ring-opening polymerization yielding filaceous cellulose whisker-graft-polycaprolactone nanocrystals (CW-g-PCL), which were incorporated into poly(lactic acid) (PLA) as a matrix[36]. The thus prepared reinforcing elements showed superior enhancing power of the mechanical performance of PLA-based materials compared to platelet-like nanoparticles of starch-g-PCL. The loading level of CW-g-PCL was varied and 8 wt% was found to be the optimal value, since with such loading, a simultaneous enhancement of the strength and the elongation was the highest ones. In fact, approximately 1.9- and 10.7-fold, increasing factors for the strength and the elongation were, respectively, reached, one compared with the values related to the neat PLA material.

An elegant way of valorising industrial crops was the preparation of cellulose cassava bagasse nanofibrils (CBN) reinforced cassava starch (CS), both being industrial by-products[37]. The morphological structure of the ensuing nanoparticles was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), presence of other components such as sugars by high performance liquid chromatography (HPLC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The resulting CBN displayed a relatively low degree of crystallinity. Their morphological characteristics were the following: a thickness of around 2-11 nm and a length of 360-1700 nm. The extracted CBN were incorporated into a thermoplastic cassava starch matrix plasticized by either glycerol or a mixture of glycerol/sorbitol (1:1). The CBN-based nanocomposite films were prepared using a melting process. The mechanical performances of the prepared nanocomposites films were evaluated by dynamical mechanical analysis (DMA) and tensile tests. They were found to depend on the nature of the plasticizer employed. In fact, when starch was plasticized by glycerol/sorbitol, the ensuing nanocomposites displayed weak performances because of the transcrystallization of amylopectin at the CBN surface. On another hand, when the matrix was plasticized by glycerol, a side events occurred and consisted of an over plasticization effect arising from sugars produced by starch hydrolysis during the acid extraction. These features were evidenced by the reduction of the glass transition temperature of starch after the incorporation of CBN and by the increase of elongation at break in tensile test. Finally, CBN-based thermoplastic starch composites displayed a lower hydrophilic character, especially for glycerol plasticized samples.

Polydisperse platelet nanocrystals were extracted from amylopectin-rich native starch granules, which were submitted to a mild acid hydrolysis yielding insoluble residues[38]. These nano-elements were isolated and characterised, which revealed that they have retained the allomorphic type of the parent granules. The two major groups of dextrins found in the prepared nanocrystals were isolated and characterized, using β-amylase and debranching enzymes (isoamylase and pullulanase) in combination with anion-exchange chromatography. The chain lengths of the dextrins in both groups were found to correspond to the thickness of the crystalline lamellae in the starch granules. About 62 mol% of the group of smaller dextrins possessed linear structure with an average degree of polymerization (DP) of about 12. The remaining fraction consisted of branched dextrins with a larger DP, i.e. close to 32. The action of the debranching enzymes was found to be inefficient towards many of the branch linkages. The distribution of branched molecules in the two populations of dextrins suggested that the nanocrystals possessed a regular and mainly homogeneous molecular structure.

Miniemulsion polymerization approach was applied to prepare a dispersion containing cellulose whiskers and a poly(styrene-co-hexylacrylate) matrix, producing a stable aqueous nanocomposite with a 20 wt% solid content and with a cellulose whiskers content ranging from 1 to 5 wt%, with respect to polymer[39]. Low amount of reactive silane (MPS) was added to stabilize the dispersion. The prepared nanocomposite dispersions were characterized using dynamic light scattering, transmission electron microscopy, and atomic force microscopy. Then, different nanocomposites sheets were produced by film-casting process and analyzed by differential scanning calorimetry, dynamic mechanical analysis, and tensile testing. Loading of 5 wt.% whiskers yielded a spectacular enhancement of the storage modulus above the glass transition temperature (500%).

Ramie cellulose whiskers (Figure 6) were chemically modified by organic acid chlorides with different lengths[40]. The modified surfaces were characterised by FTIR and X-ray photoelectron spectroscopy, elemental analysis, XRD and contact angle measurements. The crystallinity of the particles was not altered by the chain grafting. Grafts with C18 length were able to crystallize at the nanowhiskers surface. Composites with unmodified and grafted nanoparticles were prepared by extrusion process using low density polyethylene as matrix. The grafting and the length of the grafted chains were found to affect positively the homogeneity of the ensuing nanocomposites (Figure 7). In fact, higher is the aliphatic chain length better is the distribution of the nanoparticles within the matrix. The thermomechanical properties of processed nanocomposites were studied by differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA) and tensile tests. The elongation at break was improved when long chains were grafted at the surface of the nanoparticles. This feature was ascribed to the improved dispersion of the nanoparticles within the LDPE matrix

Sisal was used to produce nanowhiskers and microfibrillated cellulose (MFC), which were incorporated into polycaprolactone (PCL) matrix[41]. The surface of the reinforcing elements was chemically modified with *N*-Octadecyl isocyanate in order to improve their compatibilization with the polymeric matrix[42]. The PCL-reinforced with sisal whiskers or MFC films were prepared by film casting. Their thermal behaviour (*T*g, *T*m, *T*c, and degree of crystallinity) and their mechanical properties were determined using differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), and tensile tests, respectively. The chemical treatment was found to improve the ultimate properties of the nanocomposites.

Starch nanocrystals (StNs) were used to reinforce a soy protein isolate (SPI)[43] or cassava starch[44] or waterborne polyurethane[45] matrices, in order to produce a class of full-biodegradable nanocomposites. Soy protein isolate was found to be efficiently reinforced even with very low StNs loading level (<2 wt%). In fact,

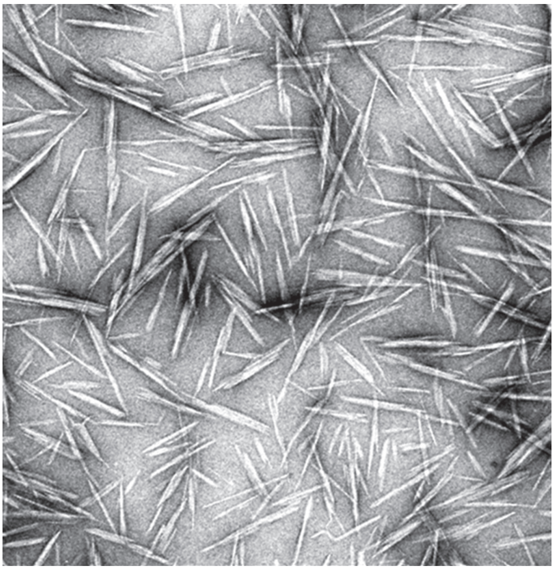


Figure 6. Transmission electron micrograph of ramie cellulose whiskers.

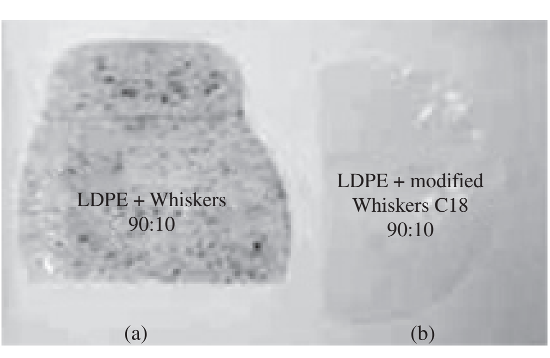


Figure 7. Photographs of the ramie cellulose whiskers reinforced low density polyethylene films: a) unmodified whiskers; and b) C18-grafted whiskers.

in this context, composites with enhanced strength and Young's modulus were produced. This was attributed to the uniform dispersion of StNs particles in the amorphous region of the SPI matrix, as well as the efficient transfer of stress mediated by interfacial interaction between the active StNs surface and the SPI matrix. Increasing the StNs content lowered their reinforcing effect since it resulted in a gradual decrease of strength and Young's modulus. This was attributed to the fact that the number and the size of StNs domains increased due to their strong self-aggregation tendency. In addition, the incorporation StNs did not alter the water uptake of the ensuing composites, since, in this context, all the materials prepared possessed similar properties to that of neat SPI material. Such behaviour could be attributed to the strong interfacial interaction between the StN fillers and the SPI matrix. When StN nanoparticles were used to reinforce cassava starch matrices, a 380% increase of the rubbery storage modulus and a 40% decrease in water vapour permeability were observed. A loading-level of 5 wt% StN-g-PCL into WPU induced an enhancement of tensile strength and elongation at break values, to compare with those of neat WPU. Higher loading levels induced the same trends, as for the other first two matrices.

Conclusions

This paper shows clearly that solid particles arising from renewable vegetal biomass from different origins, including agricultural residues and industrial crops could be viable candidates for filling and/or reinforcing different polymeric matrices. Thus, cellulose fibres, cellulose whiskers (from wood, cotton, agricultural residues and annual plants) and starch nano-platelets (from native starch granules or from industrial crops) were obtained and characterised. Their ability to undergo different surface modification was also tested and found that under specific conditions, these particles could be successfully modified yielding materials with enhanced properties. Finally, crystalline nanoparticles can be extracted directly from the biomass with different morphologies and aspect ratios allowing a multiscale approach by decreasing the size of the reinforcing elements from the micro- to the nanoscale.

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