



# Binary PVA bio-nanocomposites containing cellulose nanocrystals extracted from different natural sources: Part I



E. Fortunati<sup>a,\*</sup>, D. Puglia<sup>a</sup>, F. Luzi<sup>a</sup>, C. Santulli<sup>c</sup>, J.M. Kenny<sup>a,b</sup>, L. Torre<sup>a</sup>

<sup>a</sup> University of Perugia, Civil and Environmental Engineering Department, UdR INSTM, Strada di Pentima 4, 05100 Terni, Italy

<sup>b</sup> Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

<sup>c</sup> La Sapienza University of Rome, Chemical Engineering, Materials, and Environment Department, Via Eudossiana 18, 00184 Rome, Italy

## ARTICLE INFO

### Article history:

Received 18 February 2013

Received in revised form 11 March 2013

Accepted 20 March 2013

Available online 2 April 2013

### Keywords:

Natural fibres

Cellulose nanocrystal

Bio-nanocomposites

Poly(vinyl alcohol) (PVA)

Mechanical properties

Water absorption capacity

## ABSTRACT

PVA bio-nanocomposites reinforced with cellulose nanocrystals (CNC) extracted from commercial micro-crystalline cellulose (MCC) and from two types of natural fibres, *Phormium tenax* and *Flax* of the Belinka variety, were produced by solvent casting in water. Morphological, thermal, mechanical and transparency properties were studied while the respective efficiency of the extraction process of CNC from the three sources was evaluated. The effect of CNC types and content on PVA properties and water absorption capacity were also evaluated. Natural fibres offered higher levels of extraction efficiency when compared with MCC hydrolysis yield. Thermal analysis proved that CNC promotes the crystallization of the PVA matrix, while improving its plastic response. It was also clarified that all PVA/CNC systems remain transparent due to CNC dispersion at the nanoscale, while being all saturated after the first 18–24 h of water absorption.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

The growing interest in environment-friendly materials has motivated academic and industrial research in the development and use of biopolymers for applications in which synthetic polymers or mineral fillers are traditionally used (Armentano, Dottori, Fortunati, Mattioli, & Kenny, 2010). Moreover, bio-resources obtained from agricultural-related industries have received remarkable attention, because they can potentially serve as key components of biocomposites. The possibilities of using all the components of the fibre crop provide wide ranging opportunities for developing new applications in packaging, building, automotive, aerospace, marine, electronics, leisure and household (Anandjiwala, 2006). Plant fibres include bast, leaf and seed/fruit fibres. Bast consists of a wood core surrounded by a stem. Within the stem, there are a number of fibre bundles, each containing individual fibre cells or filaments. Examples include flax, hemp, jute, kenaf and ramie. Leaf fibres such as sisal, abaca, banana and henequen are coarser than bast fibres. Cotton is the most common seed fibre. Examples of fruit fibres include coir and oil palm. The properties of natural fibres vary considerably depending on the fibre diameter, structure, degree of polymerization, crystal structure and source, whether the fibres are taken from the plant stem,

leaf or seed, and on the growing conditions (Franco & Valadez-Gonzalez, 2005). Natural fibres have relatively high strength, high stiffness, and low density, but fibre properties and structures are influenced by several conditions as area of growth, its climate and age of the plant. Technical digestion of the fibre is another important factor which determines its structure and characteristic value, so the method adopted for fibres extraction from the plant stems is critical in the achievement of acceptable properties of the technical fibre. Mechanical or biological retting followed by alkali and bleaching treatments are common methods in order to obtain purified fibres (Siqueira, Bras, & Dufresne, 2010).

In this context, intensive study has been devoted to cellulose, and especially to its specific form which has revealed to be an interesting model filler in various polymer matrices, known as cellulose nanocrystals (CNC) (Silvério, Flauzino Neto, Dantas, & Pasquini, 2013a, 2013b). The main features that stimulate the use of CNC as polymer reinforcement agents are their large specific surface area (estimated to be several hundreds of  $\text{m}^2 \text{g}^{-1}$ ) and their very high modulus of elasticity (approximately 150 GPa) (Sturcová, Davies, & Eichhorn, 2005). Other attractive advantages of CNC are their low density (about  $1.566 \text{ g cm}^{-3}$ ), biocompatibility and biodegradability. Additionally, the CNC come from renewable natural sources which are very abundant and therefore low-costing (Brinchi, Cotana, Fortunati, & Kenny, 2013). Among the several methods for preparing cellulose nanostructures, the acid hydrolysis is the most well-known and widely used. This process breaks the disordered and amorphous parts of the cellulose, releasing

\* Corresponding author. Tel.: +39 0744 492921; fax: +39 0744 492950.

E-mail address: [elena.fortunati@unipg.it](mailto:elena.fortunati@unipg.it) (E. Fortunati).

single and well-defined crystals. This event is supported by the fact that the crystalline regions are insoluble in acids under conditions in which they are employed (Habibi, Lucia, & Rojas, 2010; Peng, Dhar, Liu, & Tam, 2011). Multifunctional bio-nanocomposite materials based on cellulose nanocrystals extracted from commercial microcrystalline cellulose (MCC), their surface modification and combination with an antimicrobial agent were recent investigated in our laboratory in terms of morphological, mechanical, thermal and antibacterial response (Fortunati et al., 2012a,b). Owing to the impact of the addition of cellulose nanocrystals on the barrier properties and on the migration behaviour of poly(lactic acid), PLA-based bio-nanocomposites were also investigated taking into account the possible involvement in food packaging applications (Fortunati et al., 2012c). Moreover, we recently reported the effectiveness of cellulose nanocrystal extraction from *Phormium tenax* leaf natural fibres by acid hydrolysis (Fortunati et al., 2012d), while we proved the possibility to use cellulose nanocrystals extracted from okra bahmia bast fibres as reinforcement phase in PVA biodegradable matrix (Fortunati et al., 2012e).

In the present work, PVA based bio-nanocomposites reinforced with cellulose nanocrystals extracted from commercial microcrystalline cellulose and from two types of natural fibres, *P. tenax* and *Flax* of the Belinka variety, were produced by solvent casting in water and characterized in terms of morphological, thermal, mechanical and transparency properties. The novelty of the work is the evaluation of the CNC extraction process efficiency in terms of yield, thermal and chemical properties comparing the behaviour of the natural fibres with the commercial MCC as start materials. The effect of CNC types and content on the PVA structural properties was deeply investigated and their influence on the PVA water absorption capacity evaluated taking into account the potential application in food-packaging industry.

## 2. Experimental part

### 2.1. Materials

Polyvinyl alcohol (PVA) (average Mw 124–146 kg mol<sup>-1</sup>, 99% hydrolysed) was used as matrix for the nanocomposite preparation.

Microcrystalline cellulose (MCC), supplied by Sigma–Aldrich, was used as start material in cellulose nanocrystal (CNC.MCC) synthesis.

*Phormium tenax* (harakeke) technical fibres were collected from New Zealand. Leaves were stripped and the fibre hanks were washed and then paddocked (left in an enclosed area to dry) and scutched. In a recent work, the chemical composition of *P. tenax* has been measured as being in the region of 55–65 wt% of cellulose, 30–40 wt% of non-cellulosic polymers, NCPs (mainly hemicellulose with a few percent of lignin and virtually no pectin) and around 3–5 wt% of extractives, including moisture, wax, oils, etc. (Fortunati et al., 2012d). From literature, other data are available, which extend the range of possible cellulose content from 45 to 72%, with most likely value around 55%, basically confirming the data for hemicellulose (30%), and lignin (11.2%). Besides, pectin (0.7%), water soluble substances (2.2%), and oils and waxes (0.7%) are also reported (Carr, Cruthers, Laing, & Niven, 2005).

*Technical Flax* fibres were provided by Finflax Ltd. In this work, the Belinka variety of flax, which was cultivated in Tyrnävä (Oulu, Finland) was used. Flax fibres were extracted from the plant by biotechnical retting (retting time 22 h, 0.3% enzyme concentration, straw/retting liquor ratio 1:15, retting temperature 41 °C). Vilppunen, Oksman, Mäentausta, Keskitalo, and Sohlo (1999) report a tensile strength of 800–1000 MPa for fibres extracted by a similar process, which is higher than that usually found for dew retted fibres, indicating that this enzymatic process is well-optimized.

Retted fibres were then scutched and hackled, and hackled fibres were used as starting material. A number of studies are also available dealing with chemical characterization of flax fibres. They are normally reported as including 65–75 wt% of cellulose (in some cases up to 81%) 15–25 wt% of NCPs (again mainly hemicellulose and usually no more than 2–2.5% each of lignin and pectin) and up to 8–10 wt% of extractives (Batra, 1998; Biagiotti, Puglia, & Kenny, 2004; Bledzki, Reihmane, & Gassan, 1996; Khalil, Rozman, Ahmad, & Ismail, 2000; Mohanty, Misra, & Hinrichsen, 2000).

### 2.2. Natural fibre pre-treatment

*Phormium Tenax* and *Technical Flax* natural fibres were pre-treated before the nanocrystal extraction as previously reported (Fortunati et al., 2012d). Briefly, the fibres were washed with distilled water several times and dried in an oven at 80 °C for 24 h. Then they were chopped to an approximate length of 5–10 mm. Finally a de-waxing step was carried out: boiling in a mixture toluene/ethanol (2:1, v/v) for 6 h. The fibres were filtered, washed with ethanol for 30 min and dried. Subsequently, a treatment procedure was used for cellulose extraction. Natural fibres were firstly treated with 0.7% (w/v) of sodium chlorite NaClO<sub>2</sub>; the fibres (liquor ratio 1:50) were boiled for 2 h and the solution pH was lowered to about 4 by means of acetic acid for the bleaching. A treatment with sodium bisulphate solution at 5% (w/v) was carried out and at the end of this preliminary chemical process, holocellulose ( $\alpha$ -cellulose + hemicellulose) was obtained, by the gradual removal of lignin. The holocellulose was treated with 17.5% (w/v) NaOH solution, filtered and washed with distilled water. The obtained cellulose was dried at 60 °C in a vacuum oven until constant weight.

### 2.3. Cellulose nanocrystal production

Commercial microcrystalline cellulose powder (MCC), pre-treated phormium and pre-treated flax were hydrolysed in sulphuric acid hydrolysis (64%, w/w) at 45 °C for 30 min as previously reported (Fortunati et al., 2012d). After removing of the acid, dialysis and ultrasonic treatment, an ion exchange resin (Dowex Marathon MR-3 hydrogen and hydroxide form) was added to the cellulose suspension for 48 h and then removed by filtration. CNC suspensions were neutralized by addition of 1.0% (v/v) of 0.25 mol/l NaOH. The obtained cellulose structures extracted from microcrystalline cellulose, phormium or flax fibres, were designed as CNC.MCC, CNC.phormium or CNC.flax, respectively. The final yield after the hydrolysis process was calculated as % (of initial weight) of the used start material (MCC, pre-treated phormium and pre-treated flax).

### 2.4. PVA/CNC bio-nanocomposites

Polyvinyl alcohol (PVA) nanocomposite films reinforced with cellulose nanocrystals (CNC) were prepared by solvent casting in water (Roohani et al., 2008). PVA aqueous solutions were firstly prepared. Depending on the desired nanocrystal proportion in the polymer matrix, a given amount of PVA (2 g) was dissolved in 20 ml distilled water at 80 °C for 2 h under mechanical stirring. Then, the solutions were kept under stirring to reach room temperature (RT). To obtain films with different compositions, the solutions were mixed with a specific amount of the aqueous dispersion of cellulose nanocrystals (CNC.MCC, CNC.ph or CNC.flax) and sonicated (Vibracell 75043, 750W, Bioblock Scientific) for 2 min. The resulting mixture was cast in a Teflon® and placed in a 37 °C oven to evaporate water. Bio-nanocomposite films of diameter equal to about 90 mm and 0.2–0.3 mm thick, containing 1 wt% or 5wt% of CNC.MCC, CNC.ph or CNC.flax respect to the PVA polymer matrix, were obtained. Resulting samples were designated

as PVA, PVA/1CNC\_MCC and PVA/5CNC\_MCC, PVA/1CNC\_ph and PVA/5CNC\_ph, PVA/1CNC\_flax and PVA/5CNC\_flax, respectively.

## 2.5. Characterization methods

### 2.5.1. Pristine, pre-treated and hydrolysed fibre characterization

The microstructure of pristine microcrystalline cellulose and natural fibres, the pre-treated phormium and flax fibres and the morphology and size of cellulose nanocrystals produced during the acid hydrolysis from different sources were investigated by means of field emission scanning electron microscope (FESEM, Supra 25-Zeiss). Surface morphology of the pristine phormium and flax fibres was characterized by graphite coating their fracture surface prior to observation. The pristine MCC and pre-treated fibres were swollen in distilled water before FESEM observation. A 1 wt% aqueous solution of material was stirred for 4 h at room temperature. The solution was then subjected to 1 h sonication over 12 h in 10 min intervals, in order to loosen up the cellulose particles. Few drops of the obtained suspension were cast onto silicon substrate, vacuum dried for 2 h and gold sputtered before the analysis. The cellulose nanocrystal suspension obtained after the acid hydrolysis from different start materials was directly cast on to silicon and observed by FESEM after the gold sputtering.

Thermogravimetric measurements (TGA) of start material, pre-treated phormium and flax fibres, and cellulose nanocrystals from different sources were performed by using a Seiko Exstar 6300 analyzer, in order to evaluate the effect of both pre-treatment and acid hydrolysis on the thermal behaviour of natural fibres. Heating scans from 30 to 900 °C at 10 °C min<sup>-1</sup> in nitrogen atmosphere were performed for each sample.

Fourier infrared (FT-IR) spectra of start material, pre-treated phormium and flax fibres, and cellulose nanocrystals from different sources were recorded using a Jasco FT-IR 615 spectrometer in the 400–4000 cm<sup>-1</sup> range. Few drops of CNC solution were cast on silicon wafer and investigated in transmission mode.

### 2.5.2. PVA bio-nanocomposite characterization

The microstructure of PVA bio-nanocomposite films was investigated by scanning electron microscope, FESEM, Supra 25-Zeiss. Cryo-cross sections of the bio-nanocomposites were sputtered with gold and then analyzed.

The transparency of PVA nanocomposite systems was evaluated by absorption measurements. A Perkin Elmer Instruments (Lambda 35) UV–vis spectrophotometer, working in the wavelength between 250 and 900 nm, was used in order to investigate the optical properties of the produced composites.

Fourier infrared (FT-IR) spectra of neat PVA and PVA bio-nanocomposites were also recorded using a Jasco FT-IR 615 spectrometer in the 400–4000 cm<sup>-1</sup> range. Few drops of PVA/CNC solution were cast on silicon wafer for each formulation and investigated in transmission mode.

The mechanical behaviour of neat PVA and PVA bio-nanocomposite was evaluated by tensile tests, performed on rectangular probes (100 × 10 mm<sup>2</sup>) on the basis of UNI ISO 527 with a crosshead speed of 5 mm min<sup>-1</sup>, a load cell of 500 N and an initial gauge length of 50 mm. Average tensile strength ( $\sigma_b$ ), elongation at break ( $\varepsilon_b$ ), and Young's modulus ( $E$ ) were calculated from the resulting stress–strain curves. The specimens were dried in a vacuum oven at 40 °C for 72 h, then cooled in a desiccator and immediately tested. The measurements were done at RT and at least five samples for each formulation were tested.

Differential scanning calorimeter (TA Instrument, Q200) measurements were performed in the temperature range from –25 to 240 °C, at 10 °C min<sup>-1</sup>, carrying out two heating and one cooling scan. The glass transition temperature ( $T_g$ ) was taken as the inflection point of the specific heat increment at the glass–rubber

transition while the melting temperature ( $T_m$ ) and the crystallization temperature ( $T_c$ ) was taken as the peak temperature of the endotherm and exotherm, respectively. Three samples were used to characterize each material.

The crystallinity degree was calculated as:

$$\chi = \frac{1}{(1 - m_f)} \left[ \frac{\Delta H}{\Delta H_0} \right] \times 100 \quad (1)$$

where  $\Delta H$ , is the enthalpy for melting or crystallization,  $\Delta H_0$  is enthalpy of melting for a 100% crystalline PVA sample, taken as 161.6 J g<sup>-1</sup> (Roohani et al., 2008) and  $(1 - m_f)$  is the weight fraction of PVA in the sample.

Thermogravimetric measurements (TGA) were performed by using a Seiko Exstar 6300. Heating scans from 30 to 600 °C at 10 °C min<sup>-1</sup> in nitrogen atmosphere were performed for each sample.

### 2.5.3. Water absorption test of PVA bio-nanocomposites

The water absorption capacity of the bio-nanocomposite films was measured using a plastic sheet with dimensions 20 × 10 mm. The specimens were first dried in a vacuum oven at 40 °C for 72 h, then cooled in a desiccator and immediately weighed. The conditioned specimens were fully immersed in a container filled with distilled water at room temperature. Each specimen was taken off from the container, the surface water was removed by adsorbing it on filter paper, and then weighed. The result obtained for each sample represents the average of three tests. The water absorption capacity (WAC) was calculated as:

$$\text{WAC\%} = \frac{W_A - W_I}{W_I} \times 100 \quad (2)$$

where  $W_A$  is the weight of the specimen at the adsorbing equilibrium and  $W_I$  is the initial dry weight of the specimen. Visual observation of the samples at different incubation times was also performed in order to evaluate the effect of water absorption to the dimension and shape of the specimens.

## 3. Results and discussions

### 3.1. Characterization of pre-treated natural fibres and hydrolysed cellulose structures

#### 3.1.1. Morphological investigation of cellulose structures

The microstructure and the dimensions of pristine materials, pre-treated natural fibres and hydrolysed cellulose nanocrystals were investigated by visual observation and by means FESEM investigation and the results are summarized in Fig. 1. The visual observation of the different natural sources gives an indication of the structure of the raw material. Commercial microcrystalline cellulose appears agglomerated into flakes with dimensions between 10 and 15  $\mu\text{m}$ , while the mean value diameter for pristine phormium and flax fibres is  $104 \pm 23 \mu\text{m}$  and  $130 \pm 43 \mu\text{m}$ , respectively. After the alkali and bleaching pre-treatment applied to the phormium and flax natural fibres, the obtained structures appear separated into micro-sized filaments showing a diameter reduction respect to the raw fibres (diameter  $11 \pm 3 \mu\text{m}$  and  $20 \pm 5 \mu\text{m}$  for phormium and flax, respectively). This diameter reduction is a consequence of the removal of non-fibrous components on the fibre surface (lignin and hemicellulose). As pointed out by Alemdar and Sain (2008a,b), FESEM images of phormium and flax fibres suggest the partial removal of impurities, hemicelluloses, lignin and pectin after chemical treatment, which are the cementing components around the fibre-bundles. Bleaching resulted in partial defibrillation and opening of fibre-bundles. Partial removal of cementing components and defibrillations are important steps for the subsequent nanocrystal hydrolysis. Both systems show multi-scale

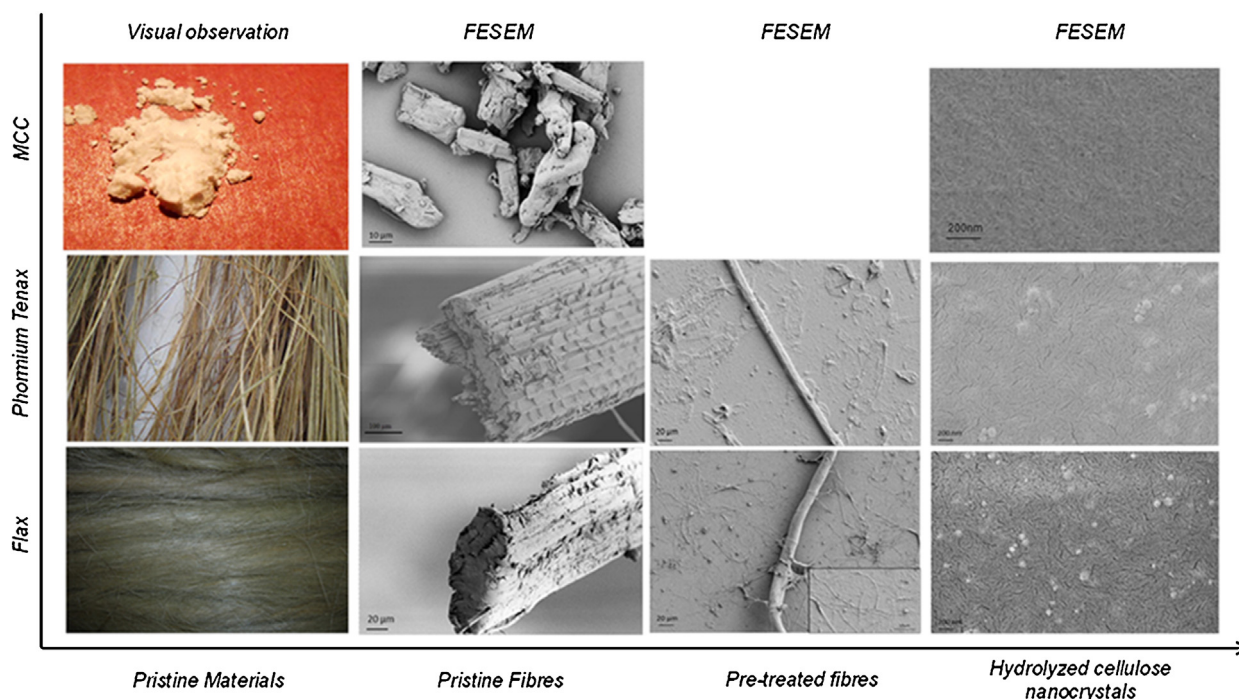


Fig. 1. Visual and morphological investigation of raw material, pre-treated fibres and hydrolysed cellulose nanocrystals from different sources.

structures, in which micro-fibres are constituted by sub-micron filaments held together by amorphous material that will be removed by the subsequent acid treatment.

The cellulose nanocrystal (CNC) suspensions were obtained from commercial microcrystalline cellulose (MCC), pre-treated phormium fibres or pre-treated flax fibres by sulphuric acid hydrolysis. The resulting cellulose nanocrystal aqueous suspension from pre-treated phormium (CNC.ph) and flax (CNC.flax) was approximately 0.3% (w/w), while the hydrolysis yield was ca. 35% for CNC.ph (Fortunati et al., 2012d) and 22% in the case of CNC.flax. For comparison, the efficiency of the MCC hydrolysis process was calculated and the resultant cellulose nanocrystal (CNC.MCC) aqueous suspension was approximately 0.5% (w/w) by weight while the calculated yield was ca. 20%, as previously reported (Fortunati et al., 2012a). High levels of efficiency were detected for the natural fibres when compared with the hydrolysis yield of commercial MCC, due to the initial elevated cellulose percentage in the raw natural materials.

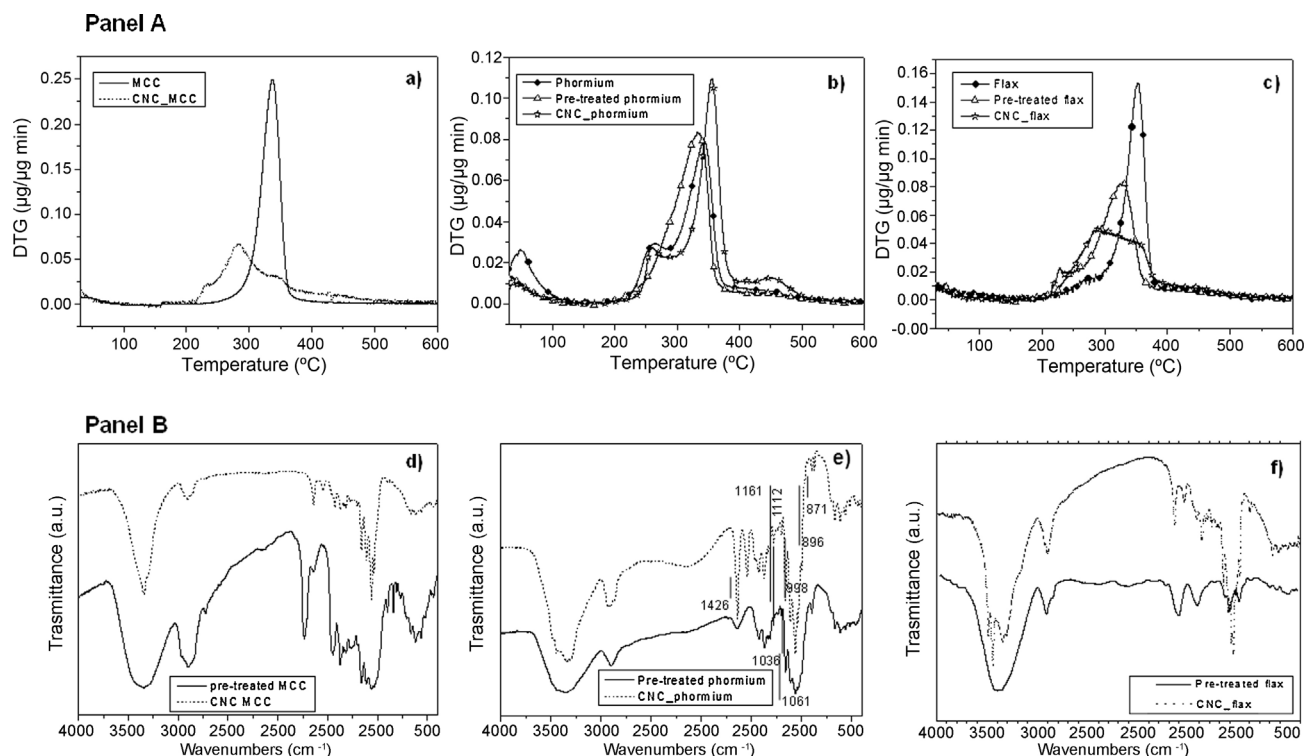
FESEM observation of cellulose nanocrystals extracted from different raw materials were performed on dried samples. A similar shape and dimensions were obtained for CNC from different sources and FESEM images for hydrolysed systems (Fig. 1) show well individualized crystals with dimensions ranging from 100 to 200 nm in length and 5–10 nm in width.

### 3.1.2. Thermal and chemical analysis of cellulose structures

Thermogravimetric tests on natural fibres shows that, a common behaviour observed for all samples is the dehydration process in which 5–8% of water is removed at low temperatures. According to the existing literature (Wielage, Lampke Th Marx, Nestler, & Starke, 1999), it has been established that there is no fibre degradation up to 160 °C. Above this temperature, thermal stability decreases and the decomposition of the fibres takes place. Fig. 2, Panel A shows the derivative curves of the three different materials (MCC, flax and phormium fibre) in the different states (pristine materials, pre-treated phormium and flax natural fibres, and hydrolysed cellulose

nanocrystals) obtained by thermal dynamic scans in nitrogen atmosphere. Decomposition of the untreated phormium fibres shows several stages, indicating the presence of different components that decompose at different temperatures. In particular, the first small peak is due to decomposition of hemicellulose, while the second major peak is due to depolymerization of cellulose (Schniewind, 1989). The rate of degradation in inert atmosphere reaches its peak at 262 and 344 °C for hemicellulose and cellulose, respectively, for untreated phormium fibre. In the case of flax fibre, the corresponding degradation temperatures are 273 and 352 °C. In MCC, the main degradation peak was observed at 337 °C, which corresponds to cellulose degradation. Thus, the presence of non-cellulosic constituents significantly controls the thermal properties of the different materials.

After the alkali pre-treatment, the peak attributed to the decomposition of hemicellulose, as expected, disappeared both for flax and phormium fibre, while a sensible reduction in the temperature of the main second peak related to cellulose was measured (333 °C for phormium, 327 °C for flax, with a similar decrease for both fibres). After the acid treatment, a substantial change in the degradation profile was observed, due to the introduction of sulphate groups that diminishes the thermal stability of the cellulose nanocrystals (Roman & Winter, 2004). It has been suggested that the degradation process of highly sulphated samples is best described in terms of two sub-processes (Araki, Wada, Kuga, & Okano, 1998; Martínez-Sanz, López-Rubio, & Lagaron, 2011): the first sub-process corresponds to the degradation of the more accessible regions, which are highly sulphated, and the second sub-process corresponds to the breakdown of the crystalline fraction which has not been attacked by sulphuric acid. In the case of CNC from phormium, the first sub-process in the DTG curve is more visible, indicating that this hydrolysis time was high enough to yield a great amount of highly sulphated regions, while in the case of CNC from flax and MCC, a small shoulder appears instead of a distinct peak indicating that, at constant hydrolysis times, the attack of the sulphuric acid was different depending on crystalline source. The DTG curve for phormium shows, when compared with



**Fig. 2.** Thermal (panel A) and chemical (panel B) characterizations of pristine materials, pre-treated fibres and hydrolysed cellulose nanocrystals from different sources.

the other two CNC sources, yields a maximum decomposition rate related to cellulose peak (0.05 and 0.07  $\mu\text{g}/\mu\text{g}$  min for CNC.flax and CNC.MCC, respectively, while the DTG value was 0.11  $\mu\text{g}/\mu\text{g}$  min for phormium).

Looking at the residual values at the end of the tests (at 600 °C), the phormium residue is always higher than flax both in raw and pre-treated state (22.5 and 19.2% for pristine phormium and flax, respectively; 29.3% and 37.1% for pre-treated phormium and flax, respectively). Shebani, van Reenen, and Meincken (2008) demonstrated that higher cellulose and lignin content in lignocellulosic materials leads to a greater thermal stability. The highest thermal stability of pre-treated phormium could be also ascribed to higher possibility of entanglements for the microfibrils. Similar increase in thermal stability due to tangling effect of flexible microfibrils has been reported by Samir, Alloin, Paillet, and Dufresne (2004). Moreover, the char residue was 28.6% in CNC.MCC and 28.3% in CNC.flax and around 24.0% for CNC.phormium. This could be due to the possible formation of acid sulphate groups on the CNC.MCC and CNC.flax, that catalyzed the dehydration reaction promoting the char formation (Scheirs, Camino, & Tumiatti, 2001; Wang, Ding, & Cheng, 2007).

Fig. 2, Panel B shows the FT-IR spectra of pre-treated flax and phormium fibre and the chemical behaviour of hydrolysed CNC.ph and CNC.flax. Moreover the FT-IR spectra of pristine MCC and CNC.flax were reported. Characteristic peaks at 1735 and 1251  $\text{cm}^{-1}$ , which are associated with hemicellulose and lignin, were not evident in the samples, indicating the removal of non-cellulosic material. It was observed that the band at 1118  $\text{cm}^{-1}$ , which could be associated to the  $-\text{C}-\text{O}-\text{C}-$  stretch of the  $\beta$ -1,4-glycosidic linkage in cellulose, was most prominent in MCC, followed by pre-treated flax. This band had a significantly low intensity in phormium, which could be due to the presence of a significant amount of non-cellulosic constituents. The band at 1352  $\text{cm}^{-1}$  can be attributed to the asymmetric  $\text{CH}_2$  bending and wagging (Sinha & Rout, 2009). The peak at 2900  $\text{cm}^{-1}$

appeared due to C–H stretching. The broad absorption in the range 3000–3600  $\text{cm}^{-1}$  can be ascribed to the stretching of H-bonded of the  $-\text{OH}$  groups, such as the peak around 1640  $\text{cm}^{-1}$  in all spectra corresponds to the absorption of water. The first band was most prominent in MCC, while this broad absorption band were smaller in phormium and flax. The peak due to the bending of hydroxyl (OH) groups bound to the cellulose structure at 1640  $\text{cm}^{-1}$  is more visible in the case of CNC.ph, while a reduced intensity is observed in the case of CNC.MCC and CNC.flax, indicating a different capability of cellulose nanocrystals to absorb water (Tserki, Zafeiropoulos, Simon, & Panayiotou, 2005). Flax and phormium fibres have significant amount of non-cellulosic constituents in their composition after the pre-treatment and this variation in the amount of non-cellulosic constituents present in the fibres influenced the H-bonding of the  $-\text{OH}$  groups considerably (Das, Ray, Bandyopadhyay, & Sengupta, 2010a).

FT-IR spectra of the CNC from the different sources show absorption bands that are all typical of cellulosic materials. The spectra analysis confirmed, for all the samples, the absence of the 1256  $\text{cm}^{-1}$  peak, suggesting the effective removal of hemicelluloses in the hydrolysed materials. The peak at 1428  $\text{cm}^{-1}$  is due to the  $-\text{CH}_2-$  bending. The increase in intensity of the band at 1035  $\text{cm}^{-1}$  indicates the presence of higher cellulose content. The small, sharp band at 895  $\text{cm}^{-1}$  represents glycosidic  $-\text{C}_1-\text{H}$  deformation, with a ring vibration contribution and  $-\text{O}-\text{H}$  bending. These features are characteristic of  $\beta$ -glycosidic linkages between the anhydroglucose units in cellulose structure (Elanthikkal, Gopalakrishnanapicker, Varghese, & Guthrie, 2010). The peaks at 1061 and 897  $\text{cm}^{-1}$  are associated with C–O stretching and C–H rock vibrations of cellulose (Alemдар & Sain, 2008a; Alemдар & Sain, 2008b), which appeared in all of the spectra. The growth of these peaks showed the increase in the percentage of cellulosic components. The signal at 871  $\text{cm}^{-1}$ , more visible in the case of CNC.ph, can be assigned to the antisymmetric out-of-phase stretching of glucose ring in cellulose, confirming the existence of cellulose nanocrystals (and their

monomeric units) after the hydrolysis treatment; moreover, the presence of signals at 1428, 1163, 1113, and 897  $\text{cm}^{-1}$  indicated that the CNC, for all the different natural sources, are primarily in the form of cellulose I (Leung et al., 2011).

### 3.2. Thermal analysis of PVA and PVA bio-nanocomposites

Differential scanning calorimetry was used to investigate the glass transition, crystallization and melting phenomena of PVA and PVA bio-nanocomposites and DSC thermal properties are summarized in Table 1. PVA film exhibited a relatively large and sharp endothermic curve with a peak at around 217 °C, while there is a specific heat increment at around 73 °C, corresponding to the glass–rubber transition of the polymer. During the cooling scan an exothermic crystallization is presented at around 189 °C in PVA film. A similar trend was detected for bio-nanocomposites at different typologies and content of cellulose nanocrystals. The glass transition temperatures of the all studied bio-nanocomposites do not change significantly respect to the polymer matrix (Fortunati et al., 2012e). The crystallinity of PVA measured during the cooling scans increases slightly with the addition of CNC and this effect is more evident at higher content of cellulose nanocrystals. A lower increase in the crystallinity value was detected for PVA/CNC.ph based systems. Moreover, an evident shift of the crystallization temperature ( $T_c$ ) to higher values was detected for all the bio-nanocomposite films with respect to the neat PVA sample. An increase of about 10 °C was detected for PVA/CNC.MCC reinforced with both 1 and 5 wt% and for the PVA/5CNC.flax system, while the  $T_c$  values were found to be close to those of the neat PVA ( $T_c = 188.94 \pm 0.24$  °C) for the PVA/CNC.ph based bio-nanocomposites. This result clearly evidences that CNC are able to promote the crystallization of the PVA matrix, acting as heterogeneous nucleating agents. A similar trend was detected also for melting temperature during the heating scan with an increase in the  $T_m$  value for CNC.MCC and CNC.flax based systems, although lower melting temperature values were measured for CNC.ph based formulations. Different types of CNC induced a diverse crystallization process in PVA matrix since this phenomenon is affected by a number of factors that include the morphology of the technical fibres (diameter, shape, dimensions of the lumens), their chemical composition and the micro-fibrillar angle of the originating plant.

Taking into account the practical application in industrial fields, one of the goals of incorporating cellulose nanocrystals into PVA matrix is to increase the temperature region where the polymer can be processed and used. For this reason, the thermal properties of bio-nanocomposite systems were also evaluated by means of thermogravimetric analysis performed in nitrogen atmosphere. Table 2 summarized the temperature values for the main degradation steps of PVA bio-nanocomposites. All the samples showed a small weight loss in the range of 35–150 °C, due to the evaporation of the water of the materials or low molecular weight compounds, while two main decomposition stages were measured for the neat PVA film and PVA based bio-nanocomposites. The second and third degradation steps were consistent with the generally accepted mechanism for the degradation of PVA (Li, Yue, & Liu, 2012). The peak temperature related to the second step of decomposition for the neat matrix was similar for the PVA/CNC bio-nanocomposites and PVA film, with the maximum degradation rate reduced with the addition of CNC to the PVA matrix up to a 5 wt% for all the CNC from different sources. The weight losses are consistent with the presence of CNC, since higher residual masses are detected with increasing CNC content, with exception of PVA/CNC.ph, where the residual values at 600 °C could be considered almost constant with the CNC content. This behaviour could be due to a reduced content of sulphate groups on the CNC.ph that confirms the trend already observed in the TGA analysis of the nanocrystals. The better results in term of thermal

**Table 1**  
Thermal properties of PVA and PVA bio-nanocomposites.

| Samples       | Cooling scan |                                   | Second heating scan |              |              |                                   | TGA           |              |                               |                              |                             |
|---------------|--------------|-----------------------------------|---------------------|--------------|--------------|-----------------------------------|---------------|--------------|-------------------------------|------------------------------|-----------------------------|
|               | $T_g$ (°C)   | $\Delta H_c$ (J g <sup>-1</sup> ) | $T_c$ (°C)          | $X_c$        | $T_g$ (°C)   | $\Delta H_m$ (J g <sup>-1</sup> ) | $T_m$ (°C)    | $X_m$        | $T_{\text{second peak}}$ (°C) | $T_{\text{third peak}}$ (°C) | Residual mass (%) at 600 °C |
| PVA           | 73.07 ± 0.11 | 48.45 ± 2.05                      | 188.94 ± 0.24       | 29.98 ± 1.27 | 76.63 ± 0.92 | 38.04 ± 3.87                      | 217.28 ± 0.05 | 23.54 ± 2.39 | 267 ± 2                       | 430 ± 3                      | 9.9                         |
| PVA/1CNC.MCC  | 72.94 ± 1.50 | 53.95 ± 1.64                      | 198.59 ± 0.51       | 33.72 ± 1.02 | 75.86 ± 0.52 | 51.97 ± 2.05                      | 222.79 ± 0.20 | 32.48 ± 1.28 | 257 ± 1                       | 432 ± 2                      | 13.0                        |
| PVA/5CNC.MCC  | 73.33 ± 1.78 | 55.82 ± 1.97                      | 200.42 ± 0.53       | 36.36 ± 1.28 | 76.98 ± 0.60 | 44.67 ± 3.51                      | 222.28 ± 0.88 | 29.09 ± 2.28 | 260 ± 2                       | 430 ± 2                      | 18.2                        |
| PVA/1CN.ph    | 75.10 ± 0.97 | 46.84 ± 4.08                      | 191.77 ± 0.12       | 30.52 ± 2.55 | 78.59 ± 0.70 | 31.70 ± 1.19                      | 215.51 ± 0.37 | 19.81 ± 0.74 | 252 ± 2                       | 428 ± 3                      | 14.1                        |
| PVA/5CNC.ph   | 72.33 ± 1.25 | 45.88 ± 3.46                      | 187.87 ± 1.21       | 32.42 ± 2.25 | 76.70 ± 0.25 | 33.10 ± 3.04                      | 211.96 ± 0.76 | 21.56 ± 1.98 | 257 ± 1                       | 430 ± 3                      | 13.7                        |
| PVA/1CNC.flax | 72.12 ± 1.34 | 47.81 ± 2.97                      | 191.72 ± 3.71       | 31.01 ± 1.85 | 76.68 ± 0.64 | 38.28 ± 5.49                      | 214.59 ± 3.66 | 23.93 ± 3.43 | 264 ± 2                       | 432 ± 2                      | 9.2                         |
| PVA/5CNC.flax | 71.83 ± 0.34 | 46.18 ± 3.76                      | 197.20 ± 0.63       | 30.48 ± 2.45 | 77.10 ± 0.72 | 39.45 ± 5.76                      | 219.12 ± 1.31 | 25.69 ± 3.75 | 250 ± 2                       | 429 ± 2                      | 16.4                        |

**Table 2**  
Results from tensile test of PVA and PVA bio-nanocomposite films.

| Samples       | $\sigma_b$ (MPa) | $\varepsilon_b$ (%) | $E_{\text{young}}$ (MPa) |
|---------------|------------------|---------------------|--------------------------|
| PVA           | 25.3 $\pm$ 4.3   | 250 $\pm$ 10        | 210 $\pm$ 15             |
| PVA/1CNC.MCC  | 36.0 $\pm$ 2.8   | 275 $\pm$ 30        | 230 $\pm$ 30             |
| PVA/5CNC.MCC  | 36.5 $\pm$ 2.0   | 300 $\pm$ 25        | 210 $\pm$ 30             |
| PVA/1CNC.ph   | 31.9 $\pm$ 5.6   | 260 $\pm$ 20        | 200 $\pm$ 30             |
| PVA/5CNC.ph   | 32.9 $\pm$ 6.1   | 340 $\pm$ 50        | 200 $\pm$ 10             |
| PVA/1CNC.flax | 37.2 $\pm$ 5.0   | 265 $\pm$ 20        | 270 $\pm$ 30             |
| PVA/5CNC.flax | 35.5 $\pm$ 4.5   | 290 $\pm$ 20        | 240 $\pm$ 30             |

stability are obtained in the case of PVA/5CNC.MCC and PVA/5CNC.flax, as expected, confirming the investigate thermal behaviour of CNC.MCC and CNC.flax.

### 3.3. Mechanical behaviour of PVA bio-nanocomposites

Tensile tests of PVA and PVA bio-nanocomposite films were performed at room temperature. The results summarized in Table 2 highlight that the addition of different kinds of CNC in PVA matrix corresponded to a general increase in the mechanical response of the systems, as the cellulose nanocrystals acted as load bearing components. Cellulose nanocrystals are able to improve the plastic response of the material, as shown by the increase of the elongation at break values for all the CNC based bio-nanocomposites respect to the PVA matrix. This result is of great importance because it was expected that the addition of CNC, able to interact with hydrophilic polymers like PVA, can restrict the polymer matrix motion reducing the elongation. The increased plastic response was more evident in the case of films with 5 wt% of CNC: in particular, the greatest value of elongation at break (340%) is shown by the PVA/5CNC.ph based system. Moreover, the addition of CNC resulted in an increase in tensile strength of about 45% for PVA/CNC.MCC and PVA/CNC.flax respect to the PVA matrix. Cellulose nanocrystals are known to form a percolating network within the polymer matrix in which the stress is assumed to be transferred through crystal/crystal interaction and crystal/polymer matrix interaction. However, it is reported that cellulose nanocrystals prepared from different resources, such as hemp, rutabaga, flax and Kraft pulp, present different reinforcement attitude (Bhatnagar & Sain, 2005). Moreover, Lee et al. (2009) reported that 1 wt% loading of cellulose nanocrystals resulted in a significant increase of tensile strength (49% higher than neat PVA film), but when the CNC loading was increased to 3 and 5 wt% to the PVA matrix, the tensile strength gradually decreased, highlighting also the important effect of cellulose crystal content. The possible interaction between polymer and CNC resulted in an efficient load transfer between polymer chains and the percolating network of nanocrystals, which makes the nanocomposites stronger. In our case, a lower increase in tensile strength (about 30%) was detected for PVA/CNC.ph systems respect to the PVA matrix. This different behaviour may be due to the differences in the fibre characteristics, such as the aspect ratio, crystallinity and morphology that can influence the mechanical response (Silvério et al., 2013a,2013b). The tensile test also underlined the capacity of CNC to increase or maintain Young's modulus respect to the PVA matrix (210 MPa) and PVA/1CNC.flax showed the highest increase (270 MPa) of the elastic response. The results of mechanical section underlined the capability of the different CNC kinds and percentages to offer a tailored reinforcement effect in both the elastic and plastic region, so that, depending on the final application, the appropriate system can be selected in order to have the desired mechanical behaviour.

### 3.4. Morphological and transparency properties of PVA bio-nanocomposites

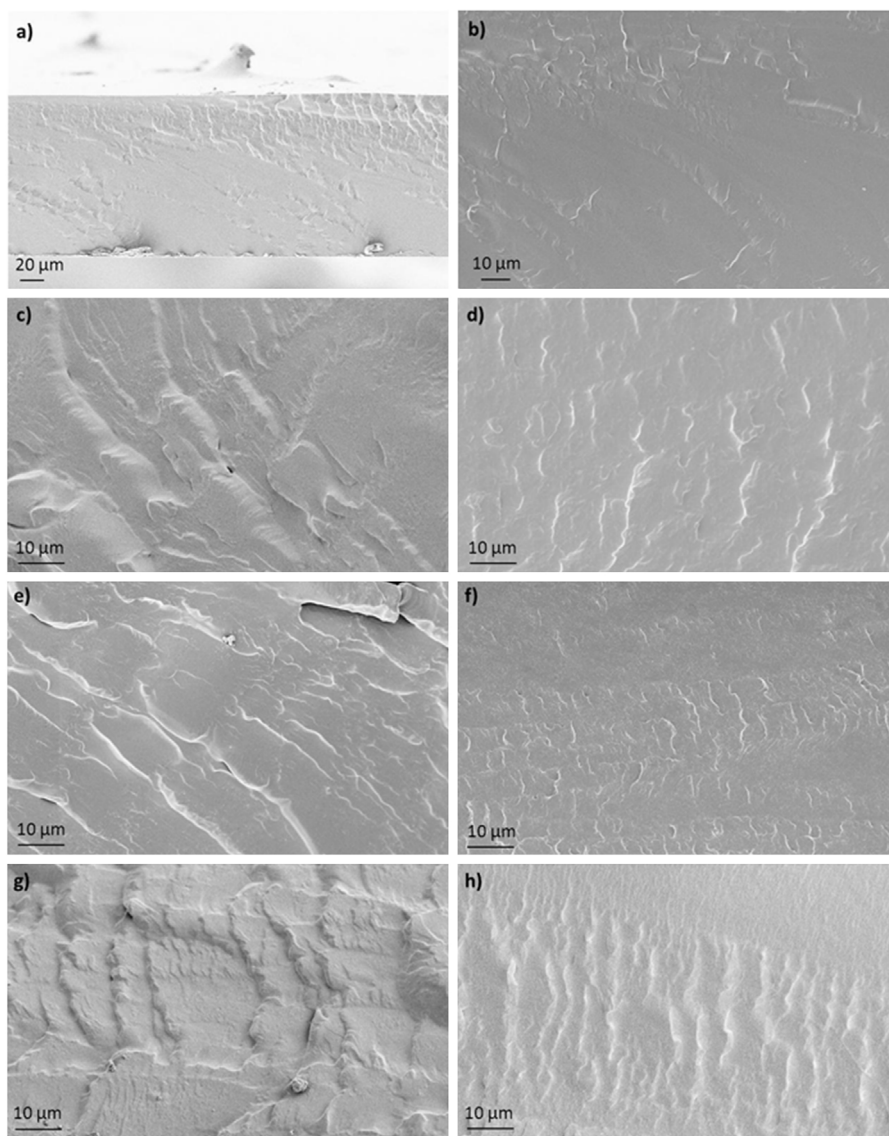
The fracture surfaces of PVA bio-nanocomposites were investigated by FESEM (Fig. 3) in order to evaluate the influence of

different typologies of cellulose nanocrystals on the microstructure of the polymer matrix. PVA film fracture surface appears smooth and uniform (Fig. 3a,b) while an increase in surface roughness was detected with the presence of cellulose nanocrystals. The aspect of the fractured surface of bio-nanocomposites appears to be more wavy respect to the PVA film and this could be ascribed to a higher degree of crystallinity of the nanocomposite material and/or to the strong interactions between the filler and the matrix (Roohani et al., 2008). No large aggregates and a homogeneous distribution of the cellulose nanocrystals in the PVA matrix were observed for the all the studied formulations implying good adhesion between the reinforcement phase and the matrix. The cellulose nanocrystals are having a tendency to aggregate due to their strong hydrogen bonding property, which leads to the formation of a percolating network-like architecture inside the matrix that is responsible for the enhanced mechanical properties of nanocomposite films. Moreover, no particular differences were induced by the crystals extracted from microcrystalline cellulose, or phormium and flax natural fibres on PVA morphology and a similar trend was detected between the bio-nanocomposites with 1 and 5 wt% of nanostructures underlined the effectiveness and efficiency of the production process. The solvent casting procedure in water guaranteed the well dispersion of cellulose nanocrystals inside the polymer matrix, avoiding the problems that occur with the use of organic solvent with cellulose nanostructures (Fortunati et al., 2012b). However, by using FESEM characterization it was difficult to identify the crystal structure due to the scale of the reinforcing phase and the low contrast between PVA and cellulose; for this reason, visual observation and transparency measurements are performed to obtain more information about the cellulose distribution inside the polymer matrix.

The results from visual observation and from the absorption UV–vis measurements shown in Fig. 4 confirm the efficiency of the processing procedure of PVA bio-nanocomposites. PVA is a transparent polymer (transmittance of 93% at a wavelength of 700 nm) and well known for their film forming properties that enable it to be used in various applications. The optical images (Fig. 4, Panel A) clearly show that the transparent nature of PVA is not affected by the addition of cellulose nanocrystals due to their nanoscaled dispersion (Fortunati et al., 2012e). All the investigated bio-nanocomposites, in fact, maintained the same transparency of the polymer matrix (Fig. 4, Panel C), without a significant reduction in the amount of light being transmitted (Fig. 4, Panel B). The uniform distribution of the colour throughout the obtained films also implies that the CNC nanocrystals were distributed uniformly within the polymer matrix. Moreover, no agglomeration effects were revealed by the visual observation (Fig. 4, Panel C) confirming the uniform CNC dispersion obtained during the processing of PVA bio-nanocomposites in water. Also in this case, no particular differences were induced by the crystals extracted by natural phormium and flax fibres when compared with the system extracted from commercial MCC on PVA transparency and a similar trend was detected between the bio-nanocomposites with 1 and 5 wt% of cellulose nanostructures. This result confirms that the combination of the chemical pre-treatment and hydrolysis process applied to natural fibres guarantees the efficiency in the production of cellulose nanocrystals with the desired dimensions and shapes if compared with the commercial MCC and this aspect allows ensuring important properties as the transparency of the polymer matrix.

### 3.5. Chemical analysis of PVA and PVA bio-nanocomposites

The chemical structure of pure PVA and PVA bio-nanocomposites was investigated by means FT-IR analysis and the results are reported in Fig. 5. The spectrum of pure PVA shows several peaks characteristics of stretching and bending vibrations



**Fig. 3.** Microstructure of PVA and PVA bio-nanocomposites.

of  $\text{—OH}$ ,  $\text{—CH}$ ,  $\text{C=C}$  and  $\text{C—O}$  groups. The pure PVA film shows peaks at  $3341\text{ cm}^{-1}$  corresponding to the hydroxyls  $\text{—OH}$  stretching, due to the strong intermolecular and intramolecular bond (Fortunati et al., 2012e),  $2940\text{ cm}^{-1}$  corresponding to the alkyl group  $\text{—CH}$  stretching,  $1735\text{ cm}^{-1}$  represents  $\text{C=O}$  and  $\text{C=C}$  stretching mode in the acetate group,  $1645\text{ cm}^{-1}$  the group  $\text{H—O—H}$  deformation mode,  $1455$  and  $1377\text{ cm}^{-1}$  corresponding to  $\text{—CH}$  bending mode,  $1248\text{ cm}^{-1}$  represents  $\text{C—O}$  bending mode in the acetate group and  $1092\text{ cm}^{-1}$  represents  $\text{C—O}$  stretching (Qua, Hornsby, Sharma, Lyons, & McCall, 2009).

The presence of cellulose nanocrystals in PVA matrix leads to the variation on the intensity of  $\text{—OH}$  stretching. This slight variation can be attributable to the interaction between  $\text{—OH}$  group on the surface of CNC and the group  $\text{—OH}$  in the PVA matrix. The addition of CNC has resulted in the appearance of two additional peaks in the spectra. The band at  $1165\text{ cm}^{-1}$  corresponds to the asymmetric ring breathing mode of cellulose while the band at  $1050\text{ cm}^{-1}$  corresponds to the  $\text{C—OH}$  bending vibrations of alcohol groups present in cellulose. This effect is more evident in the case of CNC.MCC (Fig. 5b) added at the higher content (5 wt%) in PVA. This additional band along with the characteristic peaks of PVA confirmed

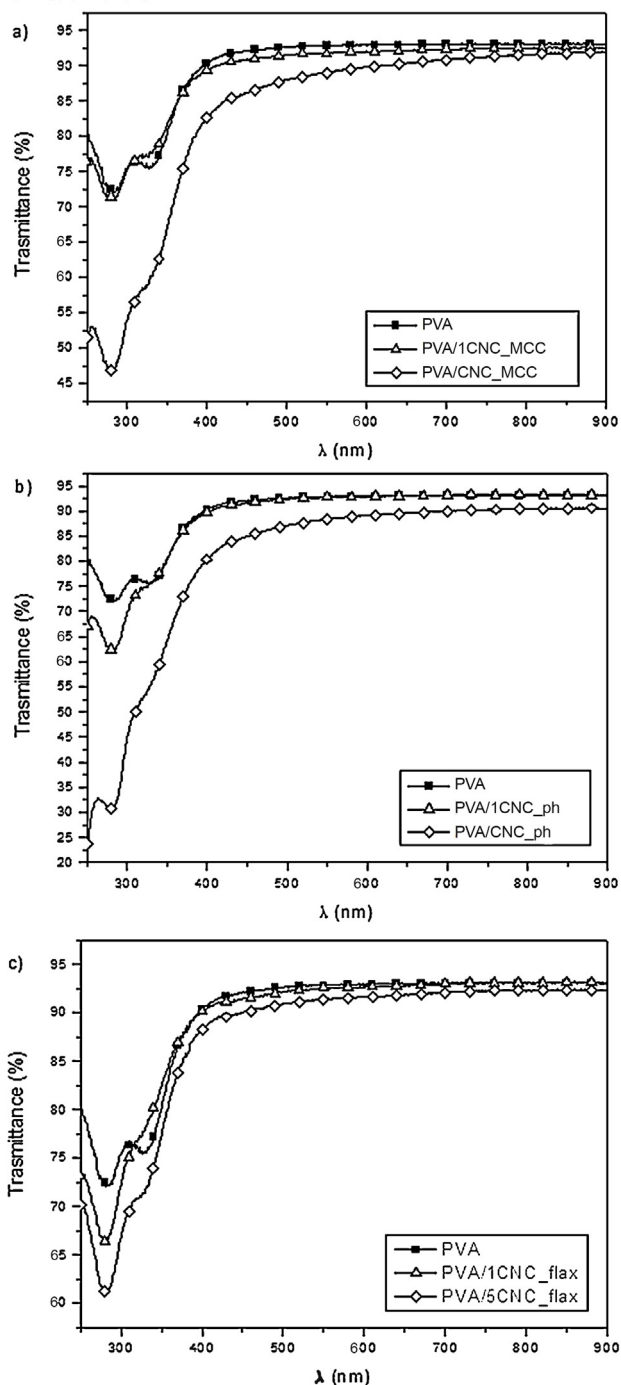
the presence of CNC in PVA and their interaction with the polymer matrix.

### 3.6. Water absorption

The water absorption capacity of PVA and PVA bio-nanocomposites was investigated in deionized water at  $25^\circ\text{C}$ . The water absorption capacity is one of the most important properties together with the biodegradability for the practical applications of the biodegradable materials and in particular for their post-use (Fortunati, Puglia, Santulli, Sarasini, & Kenny, 2012f; Fortunati et al., 2012g). The water absorbed on the materials, in fact, allows the microorganisms to grow and to utilize the material as an energy source increasing their capability to degrade when in contact with specific environments.

The kinetics of water diffusion through the PVA and PVA bio-nanocomposite films and the effect on water absorption of the type and amount of cellulose nanocrystals introduced was measured by following the weight gain of the films with time (Fig. 6). Water absorption in the film is rapid at short times ( $<24\text{ h}$ ), after which weight gain of the films due to water uptake slows down

## Panel A



## Panel B

| Samples       | Transmittance (%)<br>at $\lambda=700\text{nm}$ |
|---------------|------------------------------------------------|
| PVA           | 93.0                                           |
| PVA/1CNC_MCC  | 92.2                                           |
| PVA/5CNC_MCC  | 90.1                                           |
| PVA/1CNC_ph   | 92.8                                           |
| PVA/5CNC_ph   | 90.1                                           |
| PVA/1CNC_flax | 92.7                                           |
| PVA/5CNC_flax | 92.2                                           |



Fig. 4. Transmittance behaviour (Panel A), transmittance values at 700 nm (panel B) and visual observation (Panel C) of PVA and PVA bio-nanocomposites.

to reach a plateau value at longer times (Fig. 6). It can be noticed that the presence of cellulose nanostructures is able to increase the water absorption capacity of the PVA matrix for all formulations just after 1 h of incubation and this behaviour is more evident in the 5 wt% cellulose nanocrystal bio-nanocomposite. This effect was attributed to the increased hydrophilicity of the bio-nanocomposites due to the presence of CNC in the PVA matrix. The three-dimensional network between the nanocrystal formed by hydrogen bonding, was suggested to have a significant influence on the water absorption and swelling capability of the nanocomposites (Hossain et al., 2012). Moreover, as highlighted by the FT-IR analysis, the –OH groups on the CNC surface are able to interact

with –OH groups of the polymer chain, modifying the –OH stretching intensity of the final systems and influencing the swelling and water absorption capacity of PVA bio-nanocomposites. The presence of a higher content of CNC in the bio-nanocomposites increases the water absorption rate and PVA/5CNC based systems reach about 159% of WAC after 12 h of incubation respect to the 18 h required to the PVA/1CNC based systems to reach the same level of WAC. Furthermore, while the bio-nanocomposites reinforced with 1 wt% reach the saturation limit after 24 h of incubation, the systems reinforced with 5 wt% of CNC reach the highest value of WAC after 18 h of incubation. This different behaviour is due to the increased surface area within the bio-nanocomposites caused

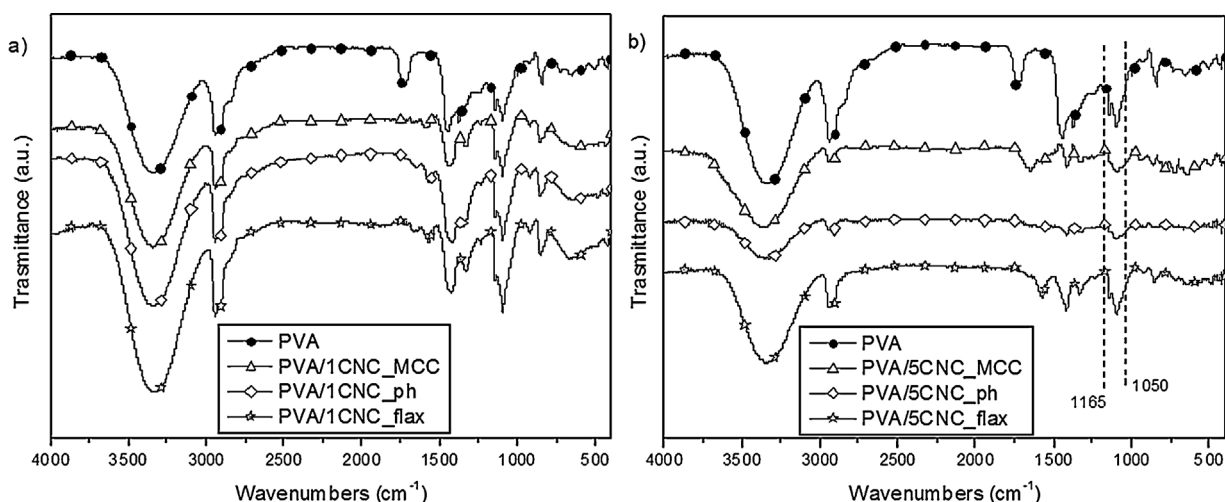


Fig. 5. Chemical analysis (FT-IR) of PVA and PVA bio-nanocomposites.

by the addition of the higher amount of CNC that allows also a water accumulation at the PVA/CNC interface. Absorbed water molecules can accumulate in three regions within the nanocomposite: in the PVA matrix, in the cellulose nanocrystals and at the polymer/cellulose interface. Crystalline cellulose does not absorb significant amounts of water and PVA water uptake is determined experimentally, leaving only the CNC/polymer interface to accommodate most part of absorbed water molecules at equilibrium (García de Rodríguez, Thielemans, & Dufresne, 2006). Moreover, lower values of WAC were detected for PVA/CNC.flax both in the case of 1 and 5 wt% of cellulose nanocrystals respect to the CNC.MCC and CNC.ph based systems. This aspect evidences a different capability of PVA to interact with water induced by the presence of CNC.flax that justifies also the different mechanical response of the studied systems. Although the specimens were

conditioned before the mechanical test, the different elastic and plastic response detected for different typologies of CNC could be also attributed to their different capability to interact with the humidity. Water diffusion and uptake can plasticize the bio-nanocomposites and increase the plastic mechanical response of the system. The higher PVA/CNC.MCC and PVA/CNC.ph sensibility in high humidity conditions, can justify the higher plastic response of these formulations if compare with PVA/CNC.flax system that showed the lowest value of WAC and also the most brittle mechanical behaviour.

Taking into account the practical use of the studied bio-nanocomposites, a visual observation of the films after the water absorption test was also carried out. Fig. 6d shows that, although an effect of swelling process is evident for each sample, all the bio-nanocomposite films are maintaining their original shape.

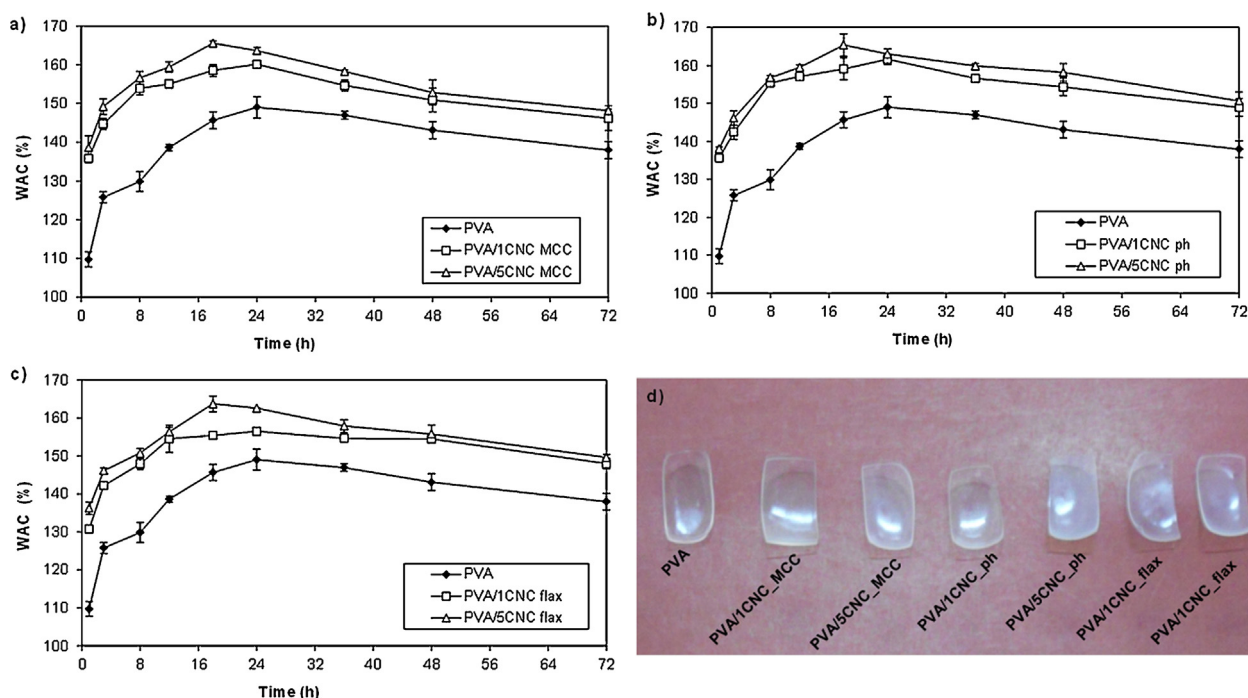


Fig. 6. Water absorption capacity of PVA and PVA bio-nanocomposites at 25 °C reinforced with CNC extracted from different sources (a–c) and visual appearance of PVA bio-nanocomposites after the water absorption test (d).

#### 4. Conclusions

PVA bio-nanocomposites reinforced with cellulose nanocrystals extracted from three different sources, one commercial (microcrystalline cellulose) and two types of natural fibres (*Phormium tenax* and Flax of the Belinka variety), were successfully produced by solvent casting in water. Morphological, thermal and chemical investigations of the obtained cellulose nanocrystals revealed that natural fibres offered high levels of extraction efficiency when compared with MCC hydrolysis yield.

No aggregates and a homogeneous distribution of the cellulose nanocrystals in the PVA matrix were observed for the all the studied formulations implying good adhesion between the reinforcement phase and the matrix and this can explain the results of thermal analysis that proved the CNC ability to promote the crystallization of the PVA matrix. The results of mechanical section underlined the capability of the different CNC kinds and percentages to offer a tailored reinforcement effect in both the elastic and plastic region, while it was clarified that all PVA/CNC systems remain transparent due to CNC dispersion at the nanoscale. The interaction of all systems with the water was deeply investigated proving that all the materials saturated after the first 18–24 h of water absorption but all the bio-nanocomposite films are able to maintain their original shape suggesting applicability also in high humidity environmental conditions.

#### Acknowledgments

E. F. acknowledges L'Oréal Italia for the fellowship "L'Oréal Italia per le Donne e la Scienza 2012" within the project "Progettazione, sviluppo e caratterizzazione di biomateriali nanostrutturati capaci di modulare la risposta e il differenziamento delle cellule staminali".

#### References

- Alemдар, A., & Sain, M. (2008a). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composites Science and Technology*, 68, 557–565.
- Alemдар, A., & Sain, M. (2008b). Isolation and characterization of nanofibers from agricultural residues—Wheat straw and soy hulls. *Bioresource Technology*, 99, 1664–1671.
- Anandjiwala, R. D. (2006). The role of research and development in the global competitiveness of natural fibre products. In *Proceedings, Natural Fibres Vision 2020* New Delhi, 8–9, December 2006, (pp. 1–15).
- Araki, J., Wada, M., Kuga, S., & Okano, T. (1998). Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose. *Colloids and Surfaces: A: Physicochemical Engineering Aspects*, 142, 75–82.
- Armentano, I., Dottori, M., Fortunati, E., Mattioli, S., & Kenny, J. M. (2010). Biodegradable polymer matrix nanocomposites for tissue engineering: A review. *Polymer Degradation and Stability*, 95, 2126–2146.
- Batra, S. K. (1998). Other long vegetable fibres. In M. Lewin, & E. M. Pearce (Eds.), *Fibre chemistry: Handbook of fibre science and technology* (pp. 505–575). New York: Marcel Dekker.
- Bhatnagar, A., & Sain, M. (2005). Processing of cellulose nanofiber-reinforced composites. *Journal of Reinforced Plastics and Composites*, 24, 1259–1268.
- Biagiotti, J., Puglia, D., & Kenny, J. M. (2004). A review on natural fibre based composites—Part I: Structure, processing and properties of vegetable fibres. *Journal of Natural Fibers*, 1, 37–68.
- Bledzki, A. K., Reihmane, S., & Gassan, J. (1996). Properties and modification methods for vegetable fibres for natural fiber composites. *Journal of Applied Polymer Science*, 59, 1329–1336.
- Brinchi, L., Cotana, F., Fortunati, E., & Kenny, J. M. (2013). Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. *Carbohydrate Polymers*, <http://dx.doi.org/10.1016/j.carbpol.2013.01.033>
- Carr, D. J., Cruthers, N. M., Laing, R. M., & Niven, B. E. (2005). Fibers from three cultivars of New Zealand flax (*Phormium tenax*). *Textile Research Journal*, 75, 93–98.
- Das, K., Ray, D., Bandyopadhyay, N. R., & Sengupta, S. (2010). Study of the properties of microcrystalline cellulose particles from different renewable resources by XRD, FTIR, nanoindentation, TGA and SEM. *Journal of Polymers and the Environment*, 18(3), 355–363.
- Elanthikkal, S., Gopalakrishnanicker, U., Varghese, S., & Guthrie, J. T. (2010). Cellulose microfibrils produced from banana plant wastes: Isolation and characterization. *Carbohydrate Polymers*, 80, 852–859.
- Fortunati, E., Armentano, I., Zhou, Q., Iannoni, A., Saino, E., Visai, L., et al. (2012). Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohydrate Polymers*, 87, 1596–1605.
- Fortunati, E., Armentano, I., Zhou, Q., Puglia, D., Terenzi, A., Berglund, L. A., et al. (2012). Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose. *Polymer Degradation and Stability*, 97, 2027–2036.
- Fortunati, E., Peltzer, M., Armentano, I., Torre, L., Jimenez, A., & Kenny, J. M. (2012). Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydrate Polymers*, 90, 948–956.
- Fortunati, E., Puglia, D., Monti, M., Peponi, L., Santulli, C., Kenny, J. M., et al. (2012). Extraction of cellulose nanocrystals from *Phormium tenax* fibres. *Journal of Polymers and Environment*, <http://dx.doi.org/10.1007/s10924-012-0543-1>
- Fortunati, E., Puglia, D., Monti, M., Santulli, C., Maniruzzaman, M., & Kenny, J. M. (2012). Cellulose nanocrystals extracted from Okra fibers in PVA nanocomposites. *Journal of Applied Polymer Science*, <http://dx.doi.org/10.1002/app.38524>
- Fortunati, E., Puglia, D., Santulli, C., Sarasini, F., & Kenny, J. M. (2012). Biodegradation of *Phormium tenax*/poly(lactic acid) composites. *Journal of Applied Polymer Science*, 125, E562–E572.
- Fortunati, E., Armentano, I., Iannoni, A., Barbale, M., Zaccaro, S., & Kenny, J. M. (2012). New multifunctional poly(lactide acid) composites: mechanical, antibacterial, and degradation properties. *Journal of Applied Polymer Science*, 124, 87–98.
- Franco, P. H. J., & Valadez-Gonzalez, M. (2005). Fibre–matrix adhesion in natural fibre composites. In A. K. Mohanty, M. Misra, & L. T. Drzal (Eds.), *Natural fibres, biopolymers and biocomposites*. Boca Raton: CRC, p. 37.
- Garcia de Rodriguez, N. L., Thielemans, W., & Dufresne, A. (2006). Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose*, 13, 261–270.
- Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews*, 110, 3479–3500.
- Hossain, K. M. K., Ahmed, I., Parsons, A. J., Scotchford, C. A., Walker, G. S., Thielemans, W., et al. (2012). Physico-chemical and mechanical properties of nanocomposites prepared using cellulose nanowhiskers and poly(lactic acid). *Journal of Materials Science*, 47, 2675–2686.
- Khalil, H. P. S. A., Rozman, H. D., Ahmad, M. N., & Ismail, H. (2000). Acetylated plant-fiber reinforced polyester composites: A study of mechanical, hygrothermal and aging characteristics. *Polymer-Plastics Technology Engineering*, 39, 757–781.
- Lee, S. Y., Mohan, D. J., Kang, I. A., Doh, G. H., Lee, S., & Han, S. H. (2009). Nanocellulose reinforced PVA composite films: Effects of acid treatment and filler loading. *Fibers and Polymers*, 10, 77–82.
- Leung, A. C. W., Hrapovic, S., Lam, E., Liu, Y., Male, K. B., Mahmoud, K. A., et al. (2011). Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small*, 7, 302–305.
- Li, W., Yue, J., & Liu, S. (2012). Preparation of nanocrystalline cellulose via ultrasound and its reinforcement capability for poly(vinyl alcohol) composites. *Ultrasonics Sonochemistry*, 19, 479–485.
- Martinez-Sanz, M., Lopez-Rubio, A., & Lagaron, J. M. (2011). Optimization of the nanofabrication by acid hydrolysis of bacterial cellulose nanowhiskers. *Carbohydrate Polymers*, 85, 228–236.
- Mohanty, A. K., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: An overview. *Macromolecular Materials Engineering*, 276, 277, 1–24.
- Peng, B. L., Dhar, N., Liu, H. L., & Tam, K. C. (2011). Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *The Canadian Journal of Chemical Engineering*, 89, 1191–1206.
- Qua, E. H., Hornsby, P. R., Sharma, H. S., Lyons, G., & McCall, R. D. (2009). Preparation and characterization of poly(vinyl alcohol) nanocomposites made from cellulose nanofibers. *Journal of Applied Polymer Science*, 113, 2238–2247.
- Roman, M., & Winter, W. T. (2004). Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules*, 5, 1671–1677.
- Roohani, M., Habibi, Y., Belgacem, N. M., Ebrahim, G., Naghi Karimi, A., & Dufresne, A. (2008). Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal*, 44, 2489–2498.
- Samir, M. A. S. A., Alloin, F., Paillet, M., & Dufresne, A. (2004). Tangling effect in fibrillated cellulose reinforced nanocomposites. *Macromolecules*, 37, 4313–4316.
- Scheirs, J., Camino, G., & Tumiatti, W. (2001). Overview of water evolution during on thermal degradation of cellulose. *European Polymer Journal*, 37, 933–942.
- Schniewind, A. P. (1989). *Concise encyclopaedia of wood and wood based materials* (1st ed.). Elmsford: Pergamon Press, pp. 271–273.
- Shebani, A. N., van Reenen, A. J., & Meincken, M. (2008). The effect of wood extracts on thermal stability of different wood species. *Thermochimica Acta*, 471, 43–50.
- Silvério, H. A., Flauzino Neto, W. P., Dantas, N. D., & Pasquini, D. (2013). Extraction and characterization of cellulose nanocrystals from corn cob for application as reinforcing agent in nanocomposites. *Industrial Crops and Products*, 44, 427–436.
- Silvério, H. A., Flauzino Neto, W. P., Dantas, N. O., & Pasquini, D. (2013). Extraction and characterization of cellulose nanocrystals from corn cob for application as reinforcing agent in nanocomposites. *Industrial Crops and Products*, 44, 427–436.
- Sinha, E., & Rout, S. K. (2009). Influence of fibre-surface treatment on structural, thermal and mechanical properties of jute fibre and its composite. *Bulletin of Materials Science*, 32, 65–76.
- Siqueira, G., Bras, J., & Dufresne, A. (2010). Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers*, 2, 728–765.
- Sturcová, A., Davies, G. R., & Eichhorn, S. J. (2005). Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules*, 6, 1055–1061.

- Tserki, V., Zafeiropoulos, N. E., Simon, F., & Panayiotou, C. (2005). A study of the effect of acetylation and propionylation surface treatments of natural fibres. *Composites Part A: Applied Science and Manufacturing*, 36, 1110–1118.
- Vilppunen, P., Oksman, K., Mäentausta, O., Keskitalo, E., & Sohlo, J. (1999). *Proceedings of the 5th International Conference on Woodfiber-Plastic Composites* (p. 309). USA: Madison.
- Wang, N., Ding, E., & Cheng, R. (2007). Thermal degradation behaviors of spherical cellulose nanocrystals with sulphate groups. *Polymer*, 48, 3486–3493.
- Wielage, B., Lampke Th Marx, G., Nestler, K., & Starke, D. (1999). Thermogravimetric and differential scanning calorimetric analysis of natural fibres and polypropylene. *Thermochimica Acta*, 337, 169–177.