REVIEW

Effect of Fiber Surface Treatments on Thermo-Mechanical Behavior of Poly(Lactic Acid)/*Phormium Tenax* Composites

F. Sarasini · D. Puglia · E. Fortunati ·
J. M. Kenny · C. Santulli

Abstract In the present study, *Phormium Tenax* fiber reinforced PLA composites were processed by injection molding and twin screw compounding with a fiber content ranging from 10 to 30 wt%. Three surface treatment methods have been used to improve the *Phormium Tenax* fiber-matrix interfacial bonding that are as follows: (1) aqueous alkaline solution, (2) silane coupling agent, and (3) a combination of alkaline and silane treatment. The mechanical, thermal and morphological properties of the resulting composites were investigated. The results have shown that the moduli of surface treated fiber reinforced composites are lower than the ones obtained for untreated composites (as a consequence of the decrease in fiber modulus caused by the chemical treatments) and no significant increase in strength was observed for any of the composites compared to neat PLA. SEM micrographs of composite fractured surfaces confirmed an improvement in the interfacial strength, which was insufficient nonetheless to significantly enhance the mechanical behavior of the resulting composites. Results from thermogravimetric analysis and differential scanning calorimetry suggest that surface treatment of Phormium affects the ability of PLA to cold crystallize, and the thermal stability of the composites at the different fiber contents was reduced with introduction of alkali and silane treated Phormium fibers.

F. Sarasini · C. Santulli
Department of Chemical Engineering Materials Environment, Sapienza-Università di Roma, UdR INSTM, Via Eudossiana 18, 00184 Rome, Italy

D. Puglia (✉) · E. Fortunati · J. M. Kenny
Civil and Environmental Engineering Department, University of Perugia, UdR INSTM, Strada di Pentima 4, 05100 Terni, Italy
e-mail: dpuglia@unipg.it

Introduction

In recent years, polymer matrices from renewable resources (biopolymers) are gaining increasing attention over traditional petroleum-based matrices (polyethylene, polypropylene, etc.) because of environmental problems related to their disposal, as well as concerns about depletion of petroleum resources [1]. Biopolymers offer environmental benefits such as biodegradability, less greenhouse gas emissions, and renewability of the base material [2]. Generally, polymers from renewable resources are classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as poly(lactic acid) (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB). Like numerous other petroleum-based polymers, many properties of biopolymers can also be improved through blending and composite approach [3]. In this regard, numerous studies have been performed for developing bio-composite materials with natural fibers and biopolymers such as starch, PLA, polycaprolactone (PCL) and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [4–8]. Natural fibers such as jute, hemp, flax, bamboo, kenaf, abaca, curaua, coir [4, 9] are commonly used as reinforcement in some recent studies. One of the most promising biopolymers is PLA, because it is made from agricultural products and is readily biodegradable. Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which in turn can be obtained by the fermentation of corn, sugar cane, sugar beet [3]. Better manufacturing practices have improved the economics of producing monomers from

agricultural feedstocks, and as such PLA is at the forefront of the emerging biodegradable plastics industries. According to a recent international market survey of biopolymers [10], existing PLA producers are planning considerable expansion of their capacity to around 800,000 t/year by 2020. PLA is currently used in the packaging field and in the production of biocompatible/bioabsorbable medical devices. PLA provides good aesthetics, strength and processability, but, because of its brittleness, it needs modification for most practical applications. One way to improve the mechanical and thermal properties of PLA-based biopolymers is to modify them by adding fillers or reinforcements [11]. In this context, together with the more traditional plant fibers increasingly used as reinforcement for polymer composites, other fibers may generate some interest, in view of their potential for this application [12]. In particular, New Zealand flax, more correctly referred to as *Phormium Tenax*, is a monocotyledon plant, belonging to the Agavaceae family, indigenous to New Zealand and Norfolk Island. During the last few years, several papers have been published concerning the use of *Phormium Tenax* fibers (extracted from the leaves) [13] as potential reinforcement in both thermoplastic and thermosetting matrices [14–18], but only a few studies regarding biodegradable thermoplastics [19–21].

It is well known that the properties of composites are significantly controlled and influenced by the interface between the reinforcement and the matrix. The strength of the filler–matrix interface is essential for stress transfer between the two components. Because of the poor interfacial adhesion in untreated natural fiber reinforced composites, much attention has been given to the modification of the fibers by physical and chemical methods [22, 23]. Shibata et al. [24] treated abaca fibers with acetic anhydride, butyric anhydride, alkali and cyanoethylation to reinforce PLA matrix by melt mixing and injection molding. They found that higher fiber content (0–20 wt%) resulted in a decreased flexural strength but in an increased flexural modulus. They also observed that fiber treatment did not significantly enhance the flexural strength and flexural modulus of abaca fiber composites. Lee et al. [25] manufactured biocomposites of kenaf fiber reinforced PLA by carding followed by treatment with silane and hot-pressing. They found that the silane coupling agent was beneficial, leading to increased flexural modulus, strength and heat deflection temperature as well as reduced water swelling. Sawpan et al. [26] manufactured chemically treated (silane and alkali treatments) short and aligned hemp fiber reinforced PLA composites by extrusion and subsequent injection molding. They also found that tensile properties (modulus and strength) and impact strength of the composites were increased with fiber treatments due to improved fiber/matrix adhesion and increased PLA crystallinity. The highest mechanical properties were obtained

with a 35 wt% aligned long alkali treated fiber composites with tensile strength of 85.4 MPa, Young's modulus of 12.6 GPa and impact strength of 7.4 kJ m^{-2}. Yu et al. [27] prepared by a two-roll mill alkali and silane treated ramie fiber reinforced poly(lactic acid) composites. Tensile, flexural and impact strength of the composites increased compared to the neat PLA, the best results being offered by alkali treated composites. Huda et al. [11] prepared composites from biodegradable poly(lactic acid) and untreated or surface treated pineapple leaf fibers (PALF) by compression molding using the film stacking method. They found that both silane and alkali treated fiber reinforced composites offered superior mechanical properties compared to untreated fiber reinforced composites. All untreated or surface treated PALF fibers significantly increased the flexural modulus of reinforced composites compared to the neat PLA matrix. In the case of 40 wt% PALF fiber content, the flexural modulus increased from 4.4 GPa for the untreated fibers to 6.0 GPa for the alkali treated fibers. There was also a slight increase in flexural strength, even though this was lower than the one of neat PLA. These studies and many others [28–31] indicate that generally modulus of PLA composites can be improved by adding fibers. However, tensile, flexural and impact strength of composites are greatly influenced by fiber type, surface treatment and processing method.

In the present study, *Phormium Tenax* fiber reinforced PLA composites were processed by injection molding and twin screw compounding with a fiber content ranging from 10 to 30 wt%. Three surface treatment methods have been used to improve the *Phormium Tenax* fiber-matrix interfacial bonding that are as follows: (1) aqueous alkaline solution, (2) silane coupling agent, and (3) a combination of alkaline and silane treatment. The mechanical, thermal and morphological properties of the resulting composites were investigated, aiming at developing fully biodegradable composites for a wide range of applications. The general objective of this study was to verify whether some chemical treatments usually applied on natural fibers improve the adhesion between PLA matrix and phormium fibers or not. A previous work [37] indicated that alkali and silane treatments can have some effect on the morphology of fiber surface, resulting on the other side in a limited degradation of the fibers themselves.

Materials and Methods

Materials

Poly(lactic acid) (PLA) 3051D, with density of 1.25 g cm^{-3}, a molecular weight (M$_n$) of about 1.42×10^4 g mol^{-1}, a melt flow index (MFI) of 7.75 g/10 min (210 °C, 2.16 kg) and a

melting temperature of 170 °C, was supplied by Nature Works®, USA. *Phormium Tenax* fibers (Ph-R) were collected from Templeton Flax Mill, Riverton, Southland, New Zealand. Leaves were stripped and the hanks of fibers were washed and then paddocked and scutched [18].

Methods

Alkali Treatment

Pre-dried fibers were mercerized in a 10 wt% sodium hydroxide (NaOH) solution at room temperature for 2 h, washed with water to remove any traces of alkali on the fiber surface, and neutralized with 1 % acetic acid solution, then dried in oven at 80 °C for 48 h (Ph-ALK). The above concentration of sodium hydroxide has been frequently used on leaf-extracted plant fibers, such as sisal, in the view of providing a fast and effective treatment to remove non-structural matter without resulting in a too extensive degradation of fiber cellulose [32].

Silane Treatment

The fibers were treated in a 2 wt% silane [(3-Aminopropyl)triethoxysilane, APTES] solution, prepared in a mixture 40/60 (wt/wt) for 45 min, washed with water to remove residual chemicals then dried in oven at 80 °C for 48 h (Ph-SIL). The same silane treatment procedure was also applied on fibers that were alkali treated previously (Ph-ALKSIL). The silane percentage applied in the literature is normally 1 %, although usually followed by application of other chemicals, such as dycumil peroxide for further bleaching [33] or executed for longer times (6 h in [34]). Here, the percentage is doubled to reduce the time of application.

Fabrication of Composites

Poly(lactic acid) (PLA) pellets and fibers were dried in a vacuum oven at 98 °C for 3 h. The PLA composites were manufactured using a twin screw microextruder (Explore 5&15 CC Micro Compounder by DSM) and mixing process parameters (50 rpm screw speed, 1 min mixing time, and temperature profile: 165–185–200 °C) were modulated to optimize the material final properties. To obtain the desired specimens for the characterizations, the molten composite samples were transferred, after the extrusion, through a preheated cylinder to a mini-injection mold (T_{mold} = 25 °C, $P_{injection}$ = 8 bar). Composites were prepared with different amount of Phormium fibers: specifically, a masterbatch containing 30 wt% of Phormium fibers respect to the polymer matrix was prepared, while the other compositions (10 and 20 wt%) were obtained diluting the master with neat PLA. Material codes for composite samples can be identified as follows: composites containing untreated Phormium are identified as PLA/Ph-R, alkali treated Phormium are identified as PLA/Ph-ALK, while silane and combined alkali-silane treatments are identified as PLA/Ph-SIL and PLA/Ph-ALKSIL, respectively. The weight content of fibers (10, 20 or 30 wt%) is indicated as PLA/10Ph-R, PLA/20Ph-R and PLA/30Ph-R, respectively.

Mechanical Properties Measurement

Tensile tests were performed in displacement control using a crosshead speed of 5 mm min^{-1} and a load cell of 30 kN by means of a digital Lloyd Instrument LR 30 K according to UNI EN ISO standard 527/2. Type 1BA sample was used for tensile measurement with an initial grip length of 54 mm. Average tensile strength, percent elongation at break, and Young's modulus (E) were calculated from the resulting stress–strain curves. The measurements were performed at room temperature and at least five samples were tested, expressing the results as mean value and standard deviation.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on 10 mg samples on a Seiko Exstar 6300 TGA quartz rod microbalance. The tests were carried out in nitrogen flow (250 ml min^{-1}) from 30 to 900 °C with a 10 °C min^{-1} heating ramp.

Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior of the matrix polymer and the composites were studied using a differential scanning calorimeter Mettler Toledo 822/e Model, calibrated with an indium sample. Dried samples (weight 10 mg) were placed in covered aluminium sample pans and then placed in the DSC sample holder. The samples were first heated at 10 °C min^{-1} in the −25–250 °C temperature range in nitrogen atmosphere (to eliminate the thermal history of the sample), then cooled at the same rate from 250 to −25 °C and heated again; the glass transition of the samples, together with peak temperatures for melting and crystallization, were evaluated and the degree of crystallinity of the sample was calculated taking as reference 93 J g^{-1} as heat of melting of the fully crystalline sample [35] according to the following Eq. 1 [36]:

$$X_c = \frac{(\Delta H_m - \Delta H_{cold})}{\Delta H_m^0 (1 - w_{fibre})} \tag{1}$$

where: ΔH_m = enthalpy of melting (J g^{-1}), ΔH_{cold} = enthalpy of cold crystallization (J g^{-1}), ΔH_m^0 = enthalpy of melting for 100 % crystalline PLA (J g^{-1}), w_{fiber} = weight fraction of Phormium fiber

Scanning Electron Microscopy (SEM)

Composite fracture surface morphology was studied using a scanning electron microscope (Philips XL40). All specimens were sputter coated with gold prior to examination to provide enhanced conductivity.

Results and Discussion

Tensile Properties of the Composites

Table 1 summarizes the tensile properties of untreated and surface treated Phormium fiber reinforced composites. All untreated or surface treated Phormium fibers significantly increased the tensile modulus of reinforced composites compared to the neat PLA matrix. This is a common finding in natural fiber reinforced composites [24, 26, 28], as the Phormium fibers are very stiff compared to PLA (Young's moduli of Phormium fiber and PLA are $\approx$ 23–27 GPa and $\approx$ 3 GPa, respectively, as reported elsewhere [13]). This behavior is likely to be due to the constraint of the matrix by the fiber under low mechanical stresses, since Young's modulus is calculated from the slope of the linear elastic part of the stress–strain curve, therefore at loads far below the failure strength of the composites. In addition, the elastic modulus does not depend to a great extent on interface adhesion and a linear increase in modulus with fiber content, according to what predicted by rule of mixtures models, was only observed in the case of untreated fiber reinforced composites. The moduli of surface treated fiber reinforced composites, despite being higher than the ones for neat PLA, are lower than the ones obtained for untreated composites. This is suggested to be the consequence of the decrease in fiber modulus caused by the chemical treatments. As reported elsewhere [37], despite the large variability in fiber diameters, a reduction of the tensile properties (strength and modulus) of Phormium fibers was equally observed for the three applied treatments. It is worthy to note that, because of the geometrical modifications they produce, chemical treatments can have an irreversible effect on the mechanical behavior of natural fibers, especially on their stiffness [11].

The failure strain of the surface treated fiber/PLA composites, as in the case of untreated fiber/PLA composites, also decreased with increasing fiber content (Table 1). This behavior could be ascribed to the lower failure strain of the fibers compared to that of PLA. Stress concentrations at the broken fiber ends could promote fracture of the matrix, leading to overall failure of the composites at strains below that of the neat PLA [7]. Moreover, elongation increased slightly by addition of surface treated Phormium fibers compared to untreated fiber reinforced composites, except for alkali treated fibers. This behavior was observed also by other authors. Sawpan and co-workers [26] obtained an increase in the failure strain for chemically treated hemp fiber reinforced PLA composites compared to untreated ones. The highest improvements were noted for combined (alkali-silane) and silane treatments, respectively. Yu et al. [27] investigated the mechanical behavior of PLA reinforced with ramie fibers treated by alkali and two different silanes. They found an increase in elongation at break of surface treated composites compared to untreated ones, with the best performance offered by the alkali treatment.

No significant increase in strength was seen for any of the composites compared to neat PLA. Slight improvement was only observed with untreated (Ph-R) and Ph-ALKSIL treated fibers. The Ph-SIL fiber reinforced composites showed the same tensile strength of neat PLA, while the worst performance was obtained for alkali treated reinforced composites, which exhibited a significant decrease in tensile strength compared to the neat matrix. In addition, the relationship between tensile strength and fiber content was not linear, so that for higher fiber content, the benefit to composite strength by adding fiber was somewhat decreased. During extrusion and injection molding of the composites containing both natural [38] and synthetic fibers [39], fiber shortening can occur due to the strong shear stresses that act in the viscous molten polymer. So, in the present case, higher fiber content resulted in an increased probability of interaction among fibers and between fibers and the equipment wall, leading to possible fiber breakage during manufacture. The likely outcome of this phenomenon is the wider presence of shorter fibers (i.e. fibers below the critical length) in the composites, which can in turn explain the reduced positive effect on tensile strength of adding fibers above a certain level. The mechanical properties of the composites depend on the fiber/matrix adhesion in addition to strength and modulus of fiber and matrix. Even though the chemical treatments can enhance the fiber/matrix adhesion, they can also adversely affect the strength and modulus of natural fibers [40, 41].

To assess the quality of fiber/matrix interface, the morphology of the fracture surface of the injection molded specimens resulting from the tensile tests was investigated using SEM. Micrographs on untreated Phormium/PLA composites (Fig. 1a) show evidence of extensive fiber pullout. It can also be observed from Fig. 1a that no matrix adhered to the surface of pulled out fibers, indicating the

Table 1 Tensile properties of untreated and surface treated Phormium fiber reinforced composites

Specimens	Tensile strength at break (MPa)	Young's modulus (GPa)	Elongation at break (%)
PLA	51.52 ± 0.66	3.04 ± 0.42	4.24 ± 0.58
PLA_20Ph-R	55.79 ± 0.99	4.69 ± 0.20	1.81 ± 0.17
PLA_30Ph-R	57.22 ± 0.22	5.66 ± 0.32	1.43 ± 0.10
PLA_10Ph-ALK	37.29 ± 5.43	4.12 ± 0.58	1.08 ± 0.25
PLA_20Ph-ALK	34.25 ± 6.09	3.69 ± 0.75	1.11 ± 0.43
PLA_30Ph-ALK	39.70 ± 11.77	4.12 ± 0.36	1.44 ± 0.92
PLA_10Ph-SIL	51.36 ± 2.44	3.86 ± 0.40	2.48 ± 0.31
PLA_20Ph-SIL	51.46 ± 0.03	4.00 ± 0.31	2.26 ± 0.21
PLA_30Ph-SIL	51.19 ± 4.75	3.93 ± 0.47	2.17 ± 0.24
PLA_10Ph-ALKSIL	55.73 ± 1.55	3.76 ± 0.92	2.58 ± 0.06
PLA_20Ph-ALKSIL	55.67 ± 0.68	4.18 ± 0.11	2.01 ± 0.08
PLA_30Ph-ALKSIL	55.63 ± 0.39	4.72 ± 0.13	1.82 ± 0.04

incompatibility between matrix and fiber. This indication is also supported by Fig. 1b where at the interface between PLA and Phormium fibers some gaps and cavities can be clearly observed. As can be seen in the fracture surface of PLA/Ph-ALK composites (Fig. 2), Ph-ALK fibers do not appear to be tightly connected to the PLA matrix as expected, so that significant pull-out is observed also in this case, especially in Fig. 2b. In the case of alkalization, the interfacial bonding mechanism between the fiber and the matrix is usually ascribed to the increase in fiber surface roughness which should result in better mechanical interlocking between fiber and matrix. Another mechanism is due to the increasing amount of cellulose exposed on the

fiber surface, thus increasing the number of possible reaction sites [42]. In addition, there are several physical and chemical modifications in the alkali treated fibers that can have divergent effects on the tensile modulus and strength. For example, the decrease in spiral angle and the increase in crystallinity, the better rearrangement of the fibrils along the load axis and the increment in the fibers aspect ratio can all act in favor of properties' enhancement. In contrast, removal of lignin and hemicellulose, which play a cementing role by transferring the stress to the microfibrils, acts against property improvement. Therefore, even though alkali treatment can give rise to better fiber/matrix adhesion (as suggested by the presence of some fibrils linking the polymer to the fibers, as shown in Fig. 2c), it can also reduce significantly the mechanical properties of single fibers. This is what is suggested to happen in the present case, where the slight improvement in fiber/matrix adhesion was not able to counterbalance effectively the disappointing effects of the treatment on natural fibers, thus resulting in a global loss of mechanical properties. In the present case, the alkali concentration could have caused excess delignification of natural fibers, resulting in a weaker or damaged fiber [43].

Silane coupling agents have been found to be effective in modifying natural fiber-polymer matrix interface and in increasing the interfacial strength [44]. During surface treatment, APTES hydrolyzes and the resultant silanol groups can bond with the natural fiber surface. Amine groups from APTES can form hydrogen bonds to COO sites on the hydrolyzed PLA backbone [11]. In this case, the silane treatment seems to promote a greater fiber/matrix adhesion, as can be seen in Fig. 3, where the fibers are better trapped by the PLA matrix and there is less evidence of fiber pull-out. Another feature was the occurrence of some fiber breakage in the plane of fracture (Fig. 3c),

Fig. 1 SEM micrographs of tensile fracture surface of untreated Phormium fiber reinforced PLA composites (PLA/30Ph-R) at different magnifications (**a**, **b**)
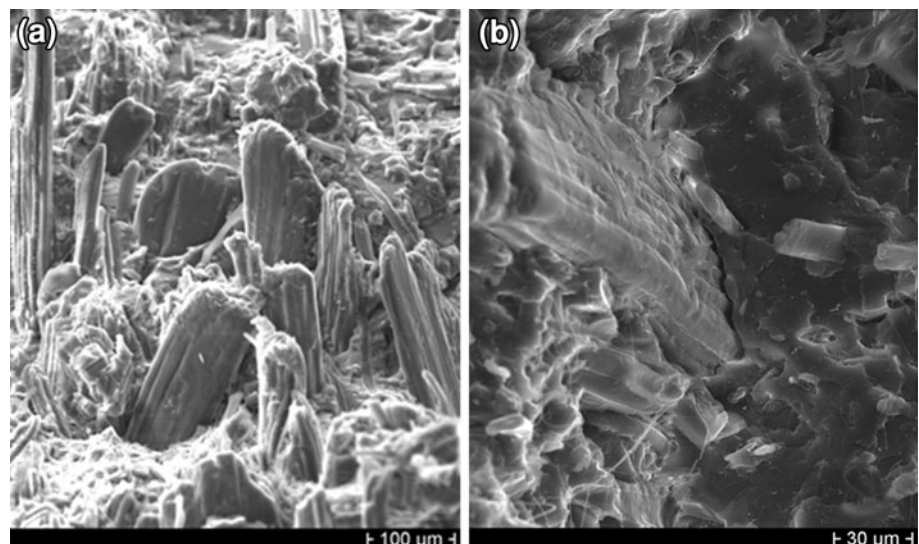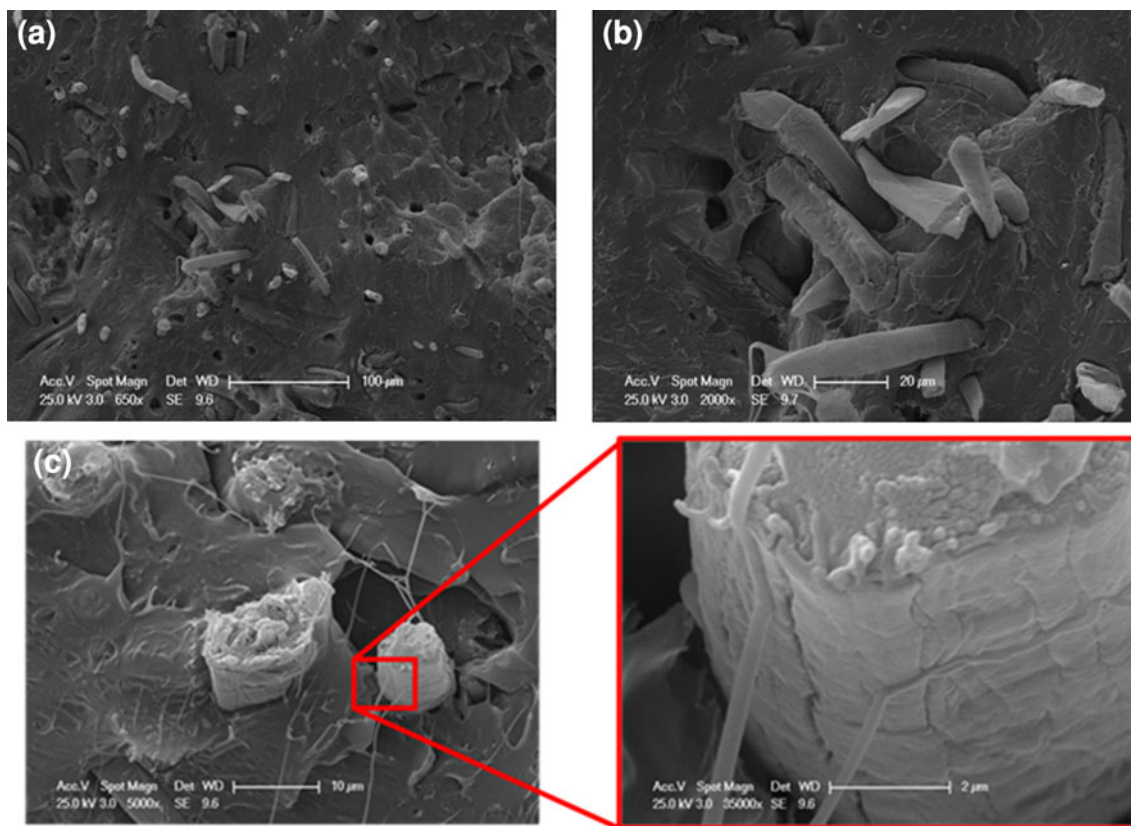
Fig. 2 SEM micrographs of tensile fracture surface of PLA/30Ph–ALK composites at different magnifications (**a–c**)

suggesting a higher degree of adhesion. Several studies in the literature confirm this trend, showing that the interaction between the silane modified fiber and the matrix is stronger than after an alkaline treatment and leads to composites with higher tensile strength for silane treated fibers than for alkaline-treated ones [42, 45]. Usually silane treatment causes little effect on the fiber tensile strength. The non optimal adhesion revealed in the present study could be explained by the fact that the process parameters for silane treatment were not optimized, a circumstance which would have minimized the condensation, leaving the silanols free to be adsorbed to the hydroxyl groups in the Phormium fibers, as found in [37]. Pre-treatment with alkali (Ph-ALKSIL), easing the accessibility toward the hydroxyl groups of the cellulose, could enhance the adhesion at the interface between fibers and neat PLA. This is confirmed by the observation of micrographs reported in Fig. 4, where the matrix well adhered or established bridges (highlighted by arrows in Fig. 4a) to the surface of pulled out fibers. This enhanced adhesion was able to offset the lower mechanical properties of the Phormium fibers. The general trend of the tensile properties of surface treated fiber reinforced composites showing no significant increase over the untreated fiber reinforced ones is not completely unexpected, as similar results can be found in literature.

Islam et al. [46] obtained no significant differences in tensile strength among random untreated short, aligned untreated short and aligned alkali treated short hemp fiber reinforced PLA composites, all of which showed additionally a lower tensile strength compared to that of neat PLA matrix. González and co-workers [47] reported no additional reinforcement effects for silane treated sisal and spent kraft fibers reinforced PLA composites.

Crystallization and Melting Behavior of the Composites

Figure 5a, b shows the DSC thermograms obtained from the first and second heating scan of Phormium based composites with 20 wt% of untreated and treated fibers (the same behavior was observed for composites at 10 and 30 wt% of reinforcement). The thermal characteristics obtained from DSC studies, related to the first and second heating scans, are summarized in Table 2. It can be seen that the PLA glass transition temperature (T_g) decreases with the addition of the fibers, while the chemical treatments slightly affected this temperature. From the analysis of the curves related to the first heating, it is possible to observe that the fibers act as nucleating agents for the neat PLA, both in the case of untreated and treated Phormium fibers, inducing lower cold crystallization temperatures (T_{cc}). This effect seems to be
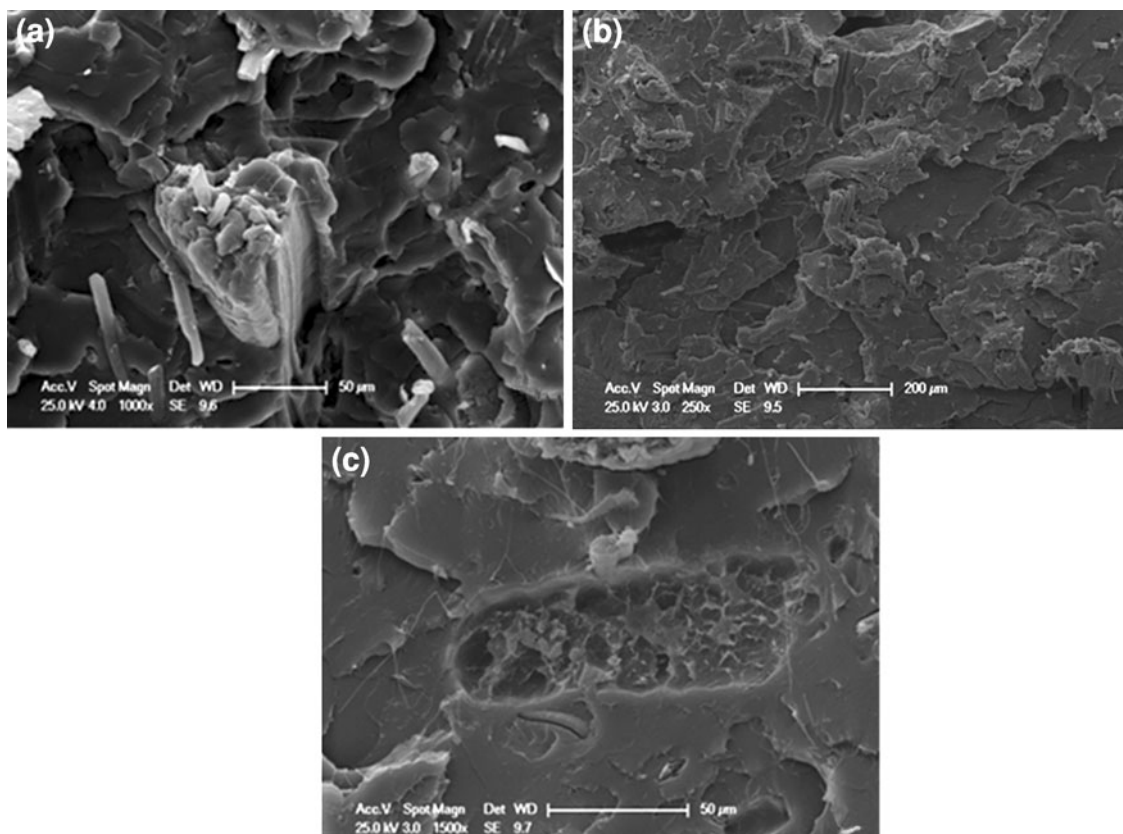
Fig. 3 SEM micrographs of tensile fracture surface at different magnifications of **a** PLA/20Ph-SIL and **b–c** PLA/30Ph-SIL composites

more evident in the case of composites based on NaOH treated Phormium (PLA/Ph-ALK and PLA/Ph-ALKSIL), for which the crystallization temperature of the composite decreases by up to 20 °C when compared to neat PLA. This means that alkali treated Phormium fibers hinder the migration and diffusion of PLA molecular chains to the surface of the nucleus in the composites, as previously reported for analogous systems [48, 49]. The behavior of aminosilane grafted Phormium fibers slightly differs from untreated fibers, even if a shift of T_{cc} at higher temperatures was observed: this is due to the fact that silane treated surface plays a retardant role in the crystallization process, which might be ascribed to the nature of interactions between the silane treated reinforcement and the PLA matrix. The interaction between the silanol groups and the polyester matrix might be responsible for decreasing the mobility of polymeric chains and increasing difficulty in crystallizing the PLA composites. This decrease of chain mobility can explain the slight increase of T_g observed in PLA/30Ph-SIL (63.0 °C) with respect to neat PLA (59.6 °C). The melting endotherms show two distinct peaks (T_{m1} and T_{m2} in Table 2) for untreated and alkali treated Phormium (Ph-ALK) fiber/PLA composites. It has been reported in the literature that a shoulder or else a low temperature peak is formed on the melting of the original crystallites as a result of lamellar rearrangement during crystallization of PLA, in particular the low temperature melting peak is generally ascribed to the melting of less perfect crystals while the high temperature one to the melting of more perfect crystals within the same lamellae [50, 51]. A general decrease for the final values of crystallinity, with respect to neat PLA and the system containing untreated Phormium, after the first heating scan (X_{c1}) was also observed, justifying the reduced mechanical performance of PLA composites in presence of surface treated Phormium fibers. In the second heating scan, neat PLA appears to be practically amorphous, which is not surprising, because a polymer with slow nucleation and crystallization rates has been selected in the first place. As regards composites, the ability to cold crystallize is confirmed only in PLA with untreated and silane treated Phormium fibers, while in the case of PLA/Ph-ALK and PLA/Ph-ALKSIL, no amorphous regions were present that were able to crystallize during the second heating scan.

Thermogravimetric Analysis of the Composites

The thermal stability of neat PLA and PLA-based composites was investigated in terms of weight loss as a function of temperature by TGA. In Fig. 6a, b, TGA
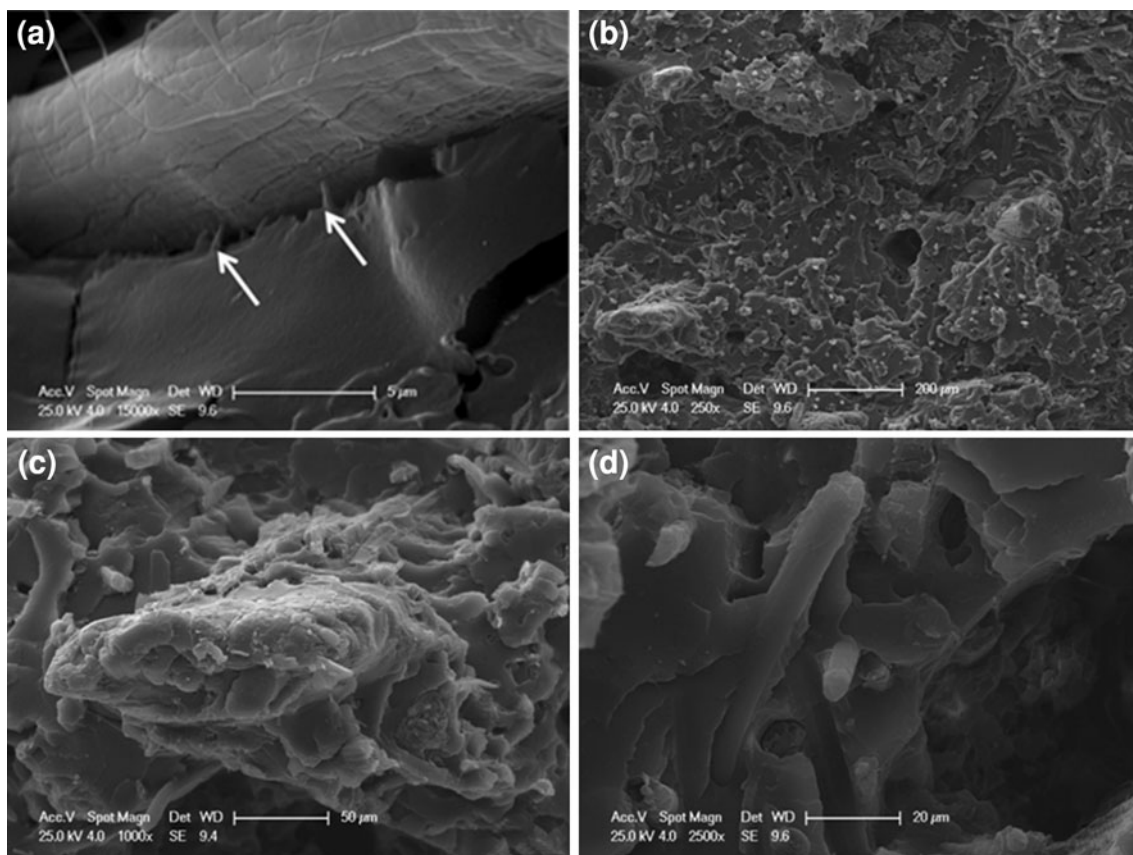
Fig. 4 SEM micrographs of tensile fracture surfaces at different magnifications of PLA/20Ph-ALKSIL (**a**) and PLA/30Ph-ALKSIL composites (**b–d**)
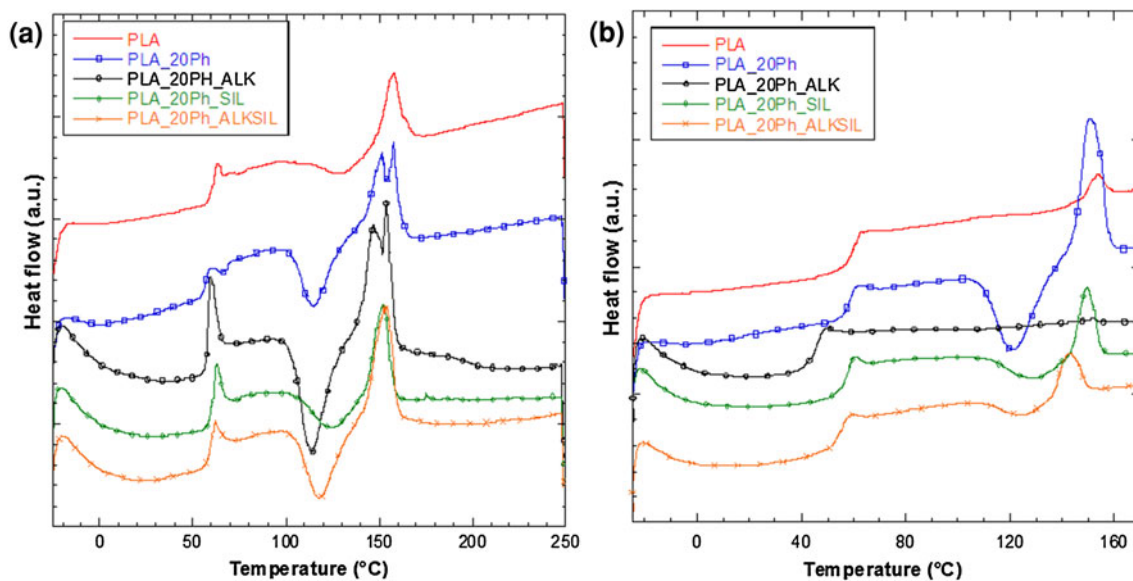

Fig. 5 Heat flow curves for the first (**a**) and second (**b**) heating cycles for PLA and PLA composites containing 20 wt% of raw and treated fibers

thermograms and DTG curves are reported for PLA and PLA composites containing 30 wt% of Phormium, both for untreated and treated fibers. Similar trend was

observed in the case of PLA composites containing 20 wt% of Phormium fibers. As it has been reported elsewhere for kenaf and PLA [52], also in the case of

Table 2 Glass transition (T_g), cold crystallization (T_{cc}) and melting peak (T_{m1} and T_{m2}) temperatures, measured degree of crystallinity (X_c) referred to the 1st and 2nd heating cycles

| Samples	1st heating scan					2nd heating scan			
	T_g (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	X_{c1} (%)	T_g (°C)	T_{cc} (°C)	T_{m1} (°C)	X_{c2} (%)
PLA	62.0 ± 3.0	129.2 ± 1.6	–	152.8 ± 4.3	8.9 ± 3.0	60.7 ± 0.6	132.3 ± 2.2	153.3 ± 0.3	1.0 ± 0.3
PLA_10Ph-ALK	61.4 ± 2.9	110.4 ± 2.8	146.8 ± 1.5	155.8 ± 0.7	2.0 ± 1.8	57.0 ± 3.7	–	–	–
PLA_10Ph-SIL	63.9 ± 1.6	125.4 ± 1.2	–	154.3 ± 2.6	0.8 ± 0.2	62.4 ± 1.0	130.4 ± 0.9	152.0 ± 1.6	2.2 ± 1.6
PLA_10Ph-ALKSIL	62.5 ± 1.7	121.8 ± 1.0	–	153.4 ± 1.2	8.8 ± 1.3	63.8 ± 0.3	131.1 ± 0.1	146.7 ± 0.1	1.8 ± 0.4
PLA_20Ph-R	59.4 ± 1.9	114.0 ± 0.5	151.0 ± 0.7	156.8 ± 1.6	6.2 ± 0.4	59.2 ± 1.9	119.8 ± 1.9	150.9 ± 2.7	1.4 ± 0.7
PLA_20Ph-ALK	61.4 ± 2.2	113.3 ± 1.1	147.2 ± 0.2	154.5 ± 0.9	3.2 ± 0.7	51.3 ± 1.2	–	–	–
PLA_20Ph-SIL	64.2 ± 2.2	125.1 ± 0.7	–	153.6 ± 1.9	6.8 ± 3.5	60.4 ± 0.8	128.9 ± 0.2	150.4 ± 1.1	1.7 ± 0.1
PLA_20Ph-ALKSIL	63.9 ± 2.0	116.8 ± 1.4	–	152.0 ± 1.9	6.0 ± 0.15	59.8 ± 0.1	125.7 ± 0.7	143.1 ± 0.3	0.3 ± 0.2
PLA_30Ph-R	57.9 ± 1.6	112.2 ± 0.6	148.6 ± 0.1	152.0 ± 0.3	1.2 ± 0.6	57.9 ± 0.2	119.2 ± 0.4	148.4 ± 0.1	1.5 ± 1.3
PLA_30Ph-ALK	63.0 ± 1.9	113.1 ± 1.6	148.3 ± 0.8	155.5 ± 0.3	0.7 ± 0.4	57.7 ± 0.5	–	–	–
PLA_30Ph-SIL	64.2 ± 1.7	127.6 ± 1.7	–	152.6 ± 0.7	6.5 ± 3.5	63.3 ± 0.4	130.1 ± 0.2	151.4 ± 0.2	0.8 ± 0.1
PLA_30Ph-ALKSIL	62.0 ± 2.3	110.2 ± 0.3	148.4 ± 0.7	157.0 ± 2.9	4.5 ± 1.3	57.4 ± 1.1	124.1 ± 0.6	140.4 ± 0.5	0.3 ± 0.2
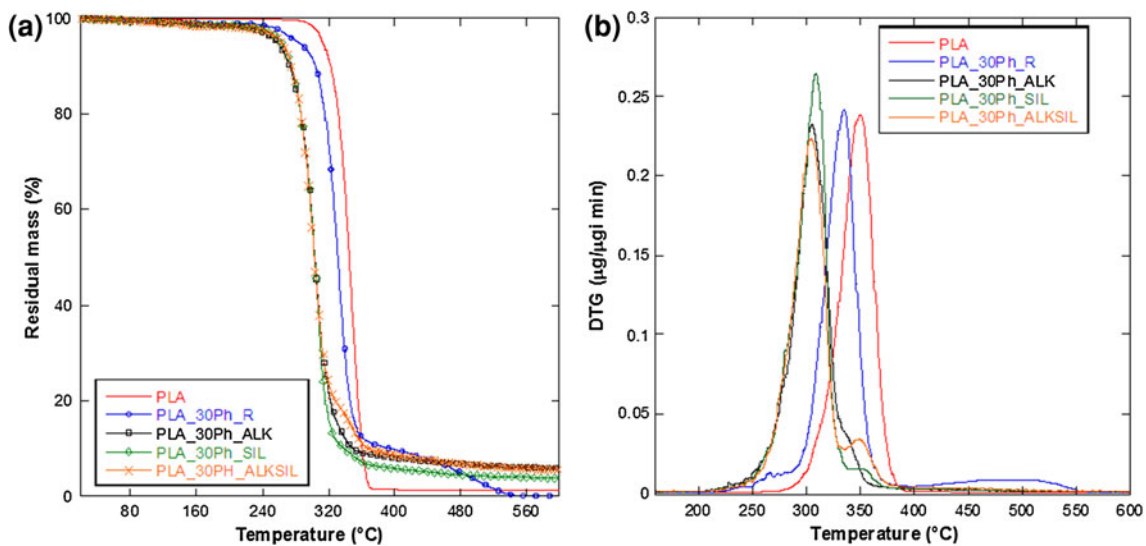
Fig. 6 Weight loss curves (**a**) and derivative curves (**b**) obtained from the TGA analysis for neat PLA and PLA containing 30 wt% of raw, alkali, silane and alkali-silane treated Phormium fibers

Phormium fibers, the degradation temperatures of the fiber and matrix are comparable. The thermal degradation of Phormium fibers occurs in two main stage process [53], where most cellulose decomposition occurs at temperature of 337.0 °C. TG curve of neat PLA shows a single step thermal degradation at a peak temperature of 350.2 °C, while lower thermal stability for all composites, compared to neat PLA, was detected. Lower maximum peak temperatures were measured for PLA/30Ph-ALKSIL and PLA/30Ph-ALK, at 304.0 and 305.5 °C, respectively, while a reduced decrease was observed for the composite containing raw fibers (335.1 °C). However, ash content appeared also to increase at the end of the test for all the treated Phormium fibers [25]. The degradation temperature of the composites with alkali treated fibers is lower than that of the composites with silane treated fibers, indicating that the stability of the interface bond between alkali treated Phormium fibers and PLA is worse than that of the interface bond between silane treated Phormium fibers and PLA. This behavior may be attributed to the lower thermal stability of the treated Phormium fibers, as previously reported in [37].

Conclusions

The investigation of the effect of different fiber surface treatments, namely alkali (Ph-ALK), silane (Ph-SIL) and a combination of the two (Ph-ALKSIL), on the behavior of PLA/Phormium fiber composites indicated that slight improvements over the tensile strength of the neat PLA matrix were only offered by untreated and Ph-ALKSIL treated fibers. This is also observed when dealing with tensile stiffness of the composites, which is somehow reduced whenever treated fibers are introduced in the polymer matrix. Both these effects appear to be more evident when increasing the amount of fibers in the composite. Despite this result, fiber-matrix adhesion was found by SEM observation to be generally increased, with the most visible improvement obtained by the combined alkali-silane treatment, which is likely to ease the accessibility of the polymer toward the hydroxyl groups of the cellulose.

All composites showed lower thermal stability with respect to PLA neat matrix. However, this negative effect appears to be generally less perceivable with the application of silane treatment than it is the case with alkali treatment. In particular, silane treatment does not reduce the ability of cold crystallization of the PLA matrix, which is revealed by untreated Phormium fibers. Also, the degradation temperature of the composites with silane treated fibers is higher than that of the composites with alkali treated fibers. This is likely to suggest that the stability of the interface bond between alkali treated Phormium fibers and PLA is weaker than that of the interface bond between silane treated Phormium fibers and PLA. However, ash content appeared also to increase at the end of the test for all the treated Phormium fibers.

The conclusion that can be drawn from the present results is that silane treatment represents an effective procedure to improve the mechanical properties of Phormium fiber reinforced PLA composites, but its success depends on many variables. As a consequence, it is very difficult to predict its effects over a particular natural system and a thorough experimental work devoted to the optimization of treatment parameters is needed.

References

1. Mohanty AK, Misra M, Drzal LT (2002) J Polym Environ 10(1/2):19
2. Ray SS, Bousmina M (2005) Prog Mater Sci 50:962
3. Yu L, Dean K, Li L (2006) Prog Polym Sci 31:576
4. Satyanarayana KG, Arizaga GGC, Wypych F (2009) Prog Polym Sci 34:982
5. Arbelaiz A, Fernandez B, Valea A, Mondragon I (2006) Carbohydr Polym 64:224
6. Bhardwaj R, Mohanty AK, Drzal LT, Pourbograt F, Misra M (2006) Biomacromolecules 7:2044
7. Bledzki AK, Jaszkiewicz A (2010) Compos Sci Technol 70:1687
8. Oksman K, Skrifvars M, Selin JF (2003) Compos Sci Technol 63:1317
9. Faruk O, Bledzki AK, Fink HP, Sain M (2012) Prog Polym Sci 37:1552
10. Market Study on Bio-based Polymers and Plastics in the World. Nova-Institute for Ecology and Innovation, 2013 (http://www.bio-based.eu/market_study/index.html)
11. Huda MS, Drzal LT, Mohanty AK, Misra M (2008) Compos Interfaces 15:169
12. Netravali AN, Chabba S (2003) Mater Today 6:22
13. De Rosa IM, Kenny JM, Puglia D, Santulli C, Sarasini F (2010) J Reinf Plast Compos 29:3450
14. Le Guen MJ, Newman RH (2007) Compos Part A 38:2109
15. Newman RH, Clauss EC, Carpenter JEP, Thumm A (2007) Compos Part A 38:2164
16. Newman RH, Le Guen MJ, Battley MA, Carpenter JEP (2010) Compos Part A 41:353
17. De Rosa IM, Santulli C, Sarasini F (2010) Mater Des 31:2397
18. Jayaraman K, Halliwell R (2009) Compos Part B 40:645
19. De Rosa IM, Iannoni A, Kenny JM, Puglia D, Santulli C, Sarasini F, Terenzi A (2011) Polym Compos 32:1362
20. Fortunati E, Puglia D, Santulli C, Sarasini F, Kenny JM (2012) J Appl Polym Sci 125:E562
21. Duchemin B, Van Luijk K, Staiger MP (2003) Proceedings of the 2nd international conference on eco-composites. Queen Mary, University of London, London, UK
22. John MJ, Anandjiwala RD (2008) Polym Compos 29:187
23. Kalia S, Kaith BS, Kaur I (2009) Polym Eng Sci 49(7):1253
24. Shibata M, Ozawa K, Teramoto N, Yosomiya R, Takeishi H (2003) Macromol Mater Eng 288:35
25. Lee BH, Kim HS, Lee S, Kim HJ, Dorgan JR (2009) Compos Sci Technol 69:2573
26. Sawpan MA, Pickering KL, Fernyhough A (2011) Compos Part A 42:310
27. Yu T, Ren J, Li S, Yuan H, Li Y (2010) Compos Part A 41:499
28. Goriparthi BK, Suman KNS, Rao NM (2012) Compos Part A 43:1800
29. Li Z, Zhou X, Pei C (2011) Int J Polym Sci. doi:10.1155/2011/803428
30. Hu R, Lim JK (2007) J Compos Mater 41:1655
31. Tokoro R, Vu DM, Okubo K, Tanaka T, Fujii T, Fujiura T (2008) J Mater Sci 43:775
32. Khanam N, Abdul Khalil HPS, Reddy GR, Naidu SV (2011) J Polym Environ 19:115
33. Herrera-Franco PJ, Valadez-González A (2005) Compos Part B 36:597
34. Khan MA, Hassan MM (2006) J Appl Polym Sci 100:4142
35. Ray SS, Yamada K, Okamoto M, Ueda K (2003) Polymer 44:857
36. Fortunati E, Armentano I, Iannoni A, Kenny JM (2010) Polym Degrad Stab 95:2200
37. Puglia D, Monti M, Santulli C, Sarasini F, De Rosa IM, Kenny JM (2013) Fiber Polym 14(3):423–427
38. Bos HL, Müssig J, van den Oever MJA (2006) Compos Part A 37:1591
39. Fu SY, Lauke B, Mader E, Yue CY, Hu X (2000) Compos Part A 31A:1117
40. Sawpan MA, Pickering KL, Fernyhough A (2011) Compos Part A 42:888
41. Alix S, Philippe E, Bessadok A, Lebrun L, Morvan C, Marais S (2009) Bioresource Technol 100:4742
42. Li X, Tabil LG, Panigrahi S (2007) J Polym Environ 15:25
43. Mishra S, Mohanty AK, Drzal LT, Misra M, Parija S, Nayak SK, Tripathy SS (2003) Compos Sci Technol 63:1377

44. Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Compos Part A 41:806
45. Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ (1999) Compos Part B 30:321
46. Islam MS, Pickering KL, Foreman NJ (2010) Compos Part A 41:596
47. González D, Santos V, Parajó JC (2012) J Thermoplast Compos 25:1005
48. Huda MS, Drzal LT, Mohanty AK, Misra M (2008) Compos Interface 15(2–3):169
49. Wu D, Wu L, Xu B, Zhang Y, Zhang M (2007) J Polym Sci Part B 45:1100
50. Sanchez MS, Mathot VBF, Poel GV, Ribelles JLG (2007) Macromolecules 40:7989
51. Eichhorn SJ, Baillie CA, Zafeiropoulos N, Mwaikambo LY, Ansell MP, Dufresne A, Entwistle KM, Herrera-Franco PJ, Escamilla GC, Groom L, Hughes M, Hill C, Rials TG, Wild PM (2001) J Mater Sci 36:2107
52. Carrasco F, Pagès P, Cañavate J (2003) Compos Sci Technol 63:161
53. Avella M, Bogoeva-Gaceva G, Bužarovska A, Errico ME, Gentile G, Grozdanov A (2008) J Appl Polym Sci 108:3542