Ramie and *Luffa cylindrica* nanowhiskers as reinforced phase in polycaprolactone

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Abstract

In the present work, nanowhiskers from ramie and *Luffa cylindrica* were used to reinforce polycaprolactone composites. We report the influence of the nanoelements' size in the mechanical and thermal properties of the composites. Chemical modifications were performed on the surface of the nanowhiskers in order to improve the compatibility with the matrix. n-Octadecyl isocyanate was used as grafting agent. Nanocomposites materials based on ramie and *Luffa cylindrica* nanocrystals (raw or chemically modified) and polycaprolactone were prepared by film casting. The extent of grafting was characterized by elementary analyses. Thermal behavior of nanocomposites was investigated with Differential Scanning Calorimetry and their mechanical properties were characterized by tensile tests and Dynamical Mechanical Analysis. The results showed the influence of filler size and amount of nanofillers. They also proved that chemical treatments improve dearly the end proprieties of the nanocomposites.

Keywords Cellulose nanowhiskers, *Luffa cylindrica*, Ramie, chemical modification, nanocomposites.

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Introduction

In the past two decades, significant attention has been devoted to the development and investigation of polymer nanocomposites, in which the incorporation of mechanically robust, high aspect ratio nanofiller considerably enhances the mechanical properties of neat polymer (Tang and Weder 2010).

The extraction of crystalline cellulosic regions, in the form of nanowhiskers, is a simple process based on acid hydrolysis. Azizi Samir et al., 2005 described cellulose whiskers as nanofibers which have been grown under controlled conditions that lead to the formation of high-purity single crystals. Many different terms have been used in the literature to designate these rod-like nanoparticles. They are mainly referred as "whiskers" or cellulose nanocrystals(Dufresne In press).

Cellulose whiskers can be prepared from a variety of sources, e.g. microcrystalline cellulose(Bondeson et al. 2006), bacterial cellulose (Hirai et al. 2009), algal cellulose (valonia) (Sugiyama et al. 1994), hemp (Cao et al. 2008), tunicin (Bonini et al. 2002, Favier et al. 1995), cotton (Thielemans et al. 2009), ramie (Habibi et al. 2008), sisal (Garcia de Rodriguez et al. 2006), sugar beet (Azizi Samir et al. 2004)], and wood (Beck-Candanedo et al. 2005).

To a certain extent, geometrical characteristics such as size, dimensions and shape of cellulose nanocrystals depend on the nature of cellulose source as well as the hydrolysis conditions such as time, temperature, ultrasound treatment, and purity of materials (Dufresne In press, Beck-Candanedo et al. 2005, Azizi Samir et al. 2005). Nevertheless, typical dimensions of whiskers range from 5 to 10 nm in diameter and from 100 to 500 nm in length. Moreover, since it is a new field of interest, it is still important to analyze and to compare the influence of different botanical sources. In this study, two important new sources have been compared. Indeed *Luffa cylindrica* has been recently studied as a potential source of whiskers (Siqueira et al. 2010a) and ramie is more and more studied in the last years (Habibi et al. 2008).

Since the cellulose whiskers are devoid of chain folding and contain only a small number of defects, their Young's modulus was determined by different authors and estimated between 130 GPa (Sakurada et al. 1962) and 250 GPa (Zimmermann et al. 2004), which is close to the modulus of the perfect crystal of native cellulose. The experimental strength was assessed to be of the order of 10 GPa (Azizi Samir et al. 2005). During last years, several strategies have been developed to adapt these cellulose nanocrystals with apolar and hydrophobic matrix. Surface grafting is one of these, and it has been used in the present work.

The main reasons to use cellulose nanowhiskers as reinforcement in polymer composites can be ascribed due to its renewability, its global presence, its huge specific surface area and impressive mechanical properties. The goal of this work is to study the mechanical properties of polycaprolactone (PCL)/whiskers nanocomposites. The influence of the source, the amount and the chemical surface modification will be detailed.

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Experimental

Materials

Ramie fibers were obtained from Stucken Melchers GmbH & Co. (Germany). Native *Luffa cylindrica* fibers, originally from Southeast Brazil, were purchased in Belo Horizonte (Minas Gerais, Brazil). Poly(caprolactone (PCL) (Mn= 42,500 g.mol^{-1}, Mw= 65,000 g.mol^{-1}). Sulfuric acid (95%), triethylamine (TEA, 99.5%), toluene (anhydrous, 99.8%), acetone (99%), and N-Octadecyl isocyanate were all obtained from Sigma–Aldrich. Dichloromethane was purchased from Chimie-Plus.

Preparation of cellulose nanowhiskers

Luffa cylindrica nanowhiskers

Luffa cylindrica fibers were cut with a FRITSCH Pulverisette mill, until fine particulate fibers were obtained. Then, it was performed a treatment with 4 wt% NaOH solution at 80 °C for 2 h under mechanical stirring. This procedure was repeated 3 times. The alkali treated fibers followed a subsequent bleaching treatment with equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water), and distilled water. The bleaching treatment was performed 4 times at 80 °C, under mechanical stirring, for 2 h. After each treatment fibers were filtered and washed with distilled water. Acid hydrolysis was achieved at 50 °C with 65 wt% sulfuric acid (pre-heated), for 40 min, using mechanical stirring. The suspension was washed with distilled water until neutrality and dialyzed with deionized water. Afterwards, the nanowhiskers suspension was homogenized with an Ultra Turrax T25 homogenizer at 10,000 rpm for 5 min and filtered in sintered glass number 1. Finally, the suspension was sonified for 3 min and stored at 4 °C.

Ramie nanowhiskers

Ramie fibers were first cut in small pieces and treated with a 2% NaOH solution at 80 °C for 2 h to remove residual additives. Then, the ramie fibers were submitted to an acid hydrolysis treatment with a 65 wt% H_2SO_4 solution at 55 °C for 30 min under continuous stirring. The suspension was washed with distilled water until neutrality and dialyzed with deionized water. The obtained suspension was homogenized with an Ultra Turrax T25 homogenizer at 13,500 rpm (2–5 min), and filtered in sintered glass number 1. After sonication for 3 min the suspension was stored at 4 °C.

Surface chemical modification. Both, ramie and *Luffa cylindrica* nanowhiskers were modified with n-octadecyl isocyanate ($C_{18}H_{37}NCO$). To achieve this reaction, a solvent exchange procedure from aqueous suspension of nanowhiskers to toluene was necessary. The surface chemical modification in toluene medium was performed in a three-necked round-bottomed flask equipped with a reflux condenser, 3 g of whiskers suspension in toluene and 100 mL of toluene were added. The system was kept under nitrogen atmosphere. An excess of n-octadecyl isocyanate (10 eq = 16.9 g) in comparison with OH groups available at the surface of a cellulosic fiber (~ 2%) was added slowly (drop by drop) when the temperature of the system reached 90 °C. The temperature was then increased up to 110 °C and it was kept in this condition for 30 min. The modified nanowhiskers were filtered and washed with ethanol to remove amine formed during the reaction and the isocyanates that did not react. Afterwards the modified material was washed with ethanol

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and centrifuged 4 times at 10,000 rpm and 10 °C for 15 min each step. The final step consisted in changing the solvent of the modified nanowhiskers from ethanol to dichloromethane(Siqueira et al. 2010b).

Processing nanocomposites

The polycaprolactone (PCL 42,500 g.mol-1) was first dissolved in dichloromethane at room temperature for 20 h (0.036 g.L-1). Different amounts of ramie and *Luffa cylindrica* nanowhiskers were used to prepare the nanocomposite films, viz. 0, 3, 6, 9 and 12 wt% on the dry basis. The corresponding amounts of nanowhiskers in dichloromethane suspensions were magnetically stirred for 6 h with the PCL solution. The suspensions were sonicated for 2 min before casting in Teflon molds, where the films were obtained by solvent evaporation at room temperature.

Characterizations

Transmission electron microscopy (TEM

A drop of diluted suspension of ramie or *Luffa cylindrica* nanowhiskers was deposited on a carbon-coated grid. The samples were stained with a 2 wt% solution of uranyl acetate, and analyzed in Philips CM200 transmission electron microscope using an acceleration voltage of 80 kV.

Elemental Analysis

Duplicate elemental analysis was carried out at the Laboratoire Central d'Analyses de Vernaison, France (CNRS). The carbon, nitrogen, and oxygen contents of cellulose naocrystals were measured independently.

Differential scanning calorimetry (DSC)

Experiments were carried out with a DSC Q100 differential calorimeter (TA Instruments) fitted with a manual liquid nitrogen cooling system. The heating and cooling rates were 10 °C.min^{-1} from -100 °C to 100 °C and from 100 °C to -100 °C, respectively, in N_2 atmosphere. Sample weights were between 6 mg and 8.5 mg.

Tensile tests

Tensile tests were carried out with a RSA3 (TA Instruments, USA) equipment with a 100 N load cell. Measurements were performed with a cross head speed of 10 mm.min^{-1} at 25 °C. Five samples were used to characterize each nanocomposite.

Dynamical mechanical analysis (DMA)

DMA of the nanocomposite films was carried out using a RSA3 (TA Instruments, USA) equipment working in tensile mode. The measurements were performed at a constant frequency of 1 Hz, strain amplitude of 0.05 %, in the temperature range from -100 °C to 80 °C, a heating rate of 5 °C.min^{-1} and a gap distance of 10 mm. The width of the samples varied from 3 to 5 mm, which were measured before each analysis. A minimum of two samples were used to characterize each nanocomposite.

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Results and discussion

Acid hydrolysis of *Luffa cylindrica* and ramie fibers leaded to aqueous suspensions of elongated nanocrystals with high aspect ratio. Figure 1 (a and b) shows electron micrographs of *Luffa cylindrica* and ramie nanowhiskers, respectively.
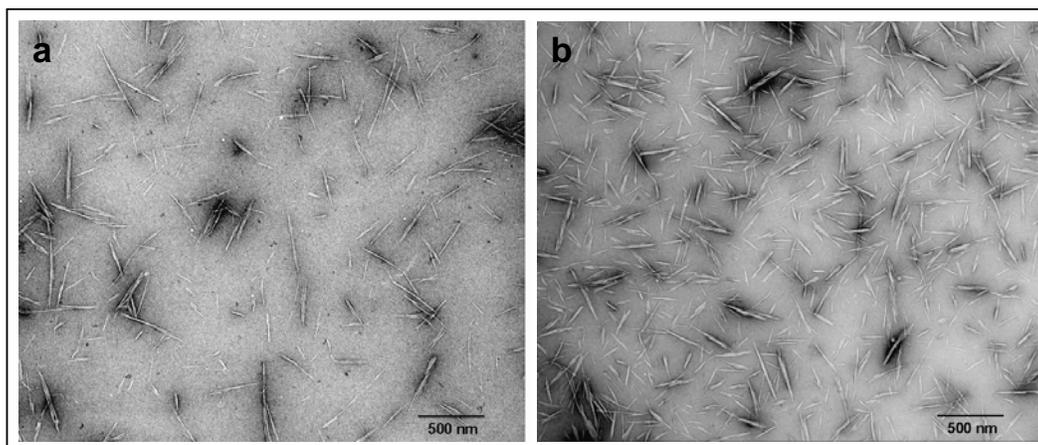

*Figure 1: Transmission electron micrographs of
(a) Luffa cylindrica and (b) ramie nanowhiskers.*

The rod-like *Luffa cylindrica* nanowhiskers exhibit an average diameter of 5.2 ± 1.3 nm and length of 242 ± 86 nm (L/d=46.5), while for ramie nanowhiskers it was found an average diameter of 7 ± 1.5 nm and length of 200 ± 80 nm (L/d=28.6). A minimum of 50 measurements were used to determine the nanowhiskers' sizes. It is worth noting that *Luffa cylindrica* whiskers present higher aspect ratio than ramie whiskers. ramie whiskers presents larger diameters than *Luffa cylindrica* ones. In both micrographs (Figure 1 a and b) well individualized and dispersed nanocrystals are observed.

The elemental analyses and the degree of substitution (DS) of unmodified and modified *Luffa cylindrica* and ramie nanowhiskers are given in Table 1.

*Table 1: Elemental analyses of unmodified and modified
Luffa cylindrica and ramie nanowhiskers.*

Samples		Experimental values				Corrected values		DS
		%C	%H	%N	%O	%C	%O	
Luffa cylindrica Whiskers	ULW	41.20	6.23	<0.10	51.27	44.44	49.38	-
	MLW	43.44	6.56	0.30	47.13	46.86	45.39	0.05
Ramie Whiskers	URW	41.31	6.41	<0.10	49.9	44.44	49.38	-
	MRW	44.61	6.68	0.30	47.06	47.99	46.57	0.07

Note: DS corresponds to the number of chains grafted per glucose unit (DS).
ULW: unmodified *Luffa cylindrica* whiskers; MLW: modified *Luffa cylindrica* whiskers; URW: unmodified ramie whiskers; and MRW: modified ramie whiskers.

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It can be observed that the DS of modified nanowhiskers are very low and under the elemental analysis technique precision. However presence of N after soxhlet extraction is observed. These results indicated chemical grafting of studied nanowhiskers.

The thermal characterization of PCL-based nanocomposite films was carried out using DSC measurements. From the analysis of DSC traces, the glass-rubber transition temperature (T_g), the melting temperature (T_m), associated heat of fusion (ΔH_m), degree of crystallinity (χ_c) and crystallization temperature (T_c) were obtained for the unfilled PCL film, and nanocomposite materials reinforced with either unmodified and modified *Luffa cylindrica* and ramie nanowhiskers The resulting experimental data are listed in Table 2.

For all nanocomposites the crystallization temperature is significantly increased (around 10 to 13 °C) compared to the neat matrix. The filler most probably acts as a nucleating agent for the crystallization of PCL. The addition of both, *Luffa cylindrica* and ramie whiskers, to the PCL matrix significantly increase the degree of crystallinity of the host matrix, regardless their modification state. It is increased from 51 wt% for the neat matrix to values around to 63 wt% for nanocomposite films regardless the filler content. This is in accordance with results were observed in a previous study with PCL-sisal nanowhiskers composites(Siqueira et al. 2009).

Concerning the melting point (T_m) of the PCL matrix, it slightly increases, when adding *Luffa cylindrica* or ramie whiskers, from about 63 °C to 64-66 °C (Table 2). This temperature is directly related to the size of the crystalline domains.

The non-linear mechanical behavior of PCL-based nanocomposite films was characterized by tensile tests performed at room temperature. Typical stress-strain curves obtained from tensile tests for PCL-based nanocomposite films are shown in Figure 2.

Mechanical properties of PCL matrix and PCL-nanocomposites reinforced by cellulose nanowhiskers at different compositions are shown in Table 3.

Table 2: Thermal characteristics of PCL-based nanocomposites obtained from DSC analysis: glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_m), degree of crystallinity (χ_c), and temperature of crystallization (T_c)

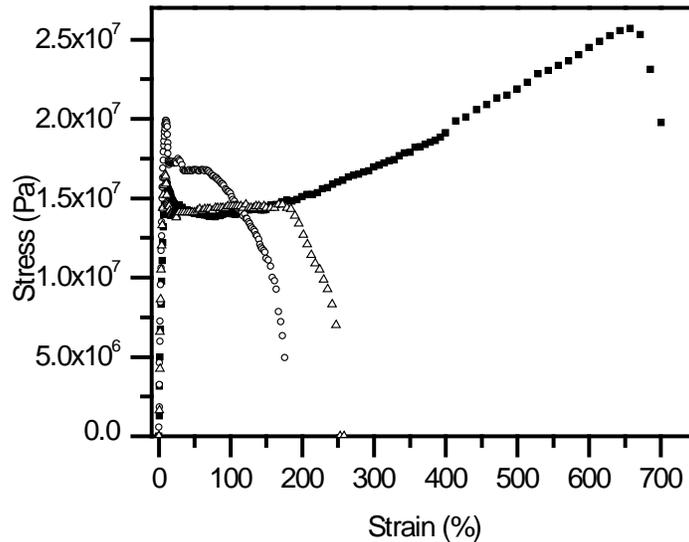| Filler	Sample	T_g (°C)	T_m (°C)	ΔH_m (J.g^{-1})	χ_c	T_c (°C)
	PCL matrix	-62.0 ± 0.23	63.4 ± 0.42	80.70 ± 0.85	0.51	22.8 ± 0.36
Unmodified Luffa Whiskers	PCL-ULW 3%	-59.19 ± 0.16	65.63 ± 0.01	84.29 ± 2.12	0.55	33.05 ± 0.16
	PCL-ULW 6%	-57.69 ± 1.62	65.29 ± 0.1.13	86.70 ± 1.49	0.58	33.67 ± 1.21
	PCL-ULW 9%	-57.41 ± 0.34	65.24 ± 0.30	80.24 ± 1.54	0.56	34.35 ± 0.84
	PCL-ULW 12%	-58.84 ± 1.17	66.09 ± 0.28	77.91 ± 2.06	0.56	35.70 ± 0.15
Modified Luffa Whiskers	PCL-MLW 3%	-59.03 ± 0.78	64.20 ± 1.21	95.29 ± 0.83	0.63	35.14 ± 0.07
	PCL-MLW 6%	-57.71 ± 0.25	64.17 ± 0.99	92.67 ± 1.33	0.63	35.08 ± 1.13
	PCL-MLW 9%	-58.01 ± 0.33	64.73 ± 0.16	88.90 ± 1.21	0.62	34.63 ± 0.25
	PCL-MLW 12%	-57.29 ± 0.33	64.90 ± 0.09	88.59 ± 2.89	0.64	35.06 ± 0.31
Unmodified Ramie Whiskers	PCL-URW 3%	-58.05 ± 0.23	64.67 ± 0.32	89.90 ± 3.35	0.59	34.16 ± 0.38
	PCL-URW 6%	-59.55 ± 0.33	64.76 ± 2.20	89.36 ± 1.49	0.61	33.25 ± 0.06
	PCL-URW 9%	-60.32 ± 1.09	65.58 ± 0.09	83.18 ± 2.79	0.58	33.79 ± 0.06
	PCL-URW 12%	-60.45 ± 1.24	65.90 ± 1.08	83.22 ± 1.51	0.60	34.37 ± 0.54
Modified Ramie Whiskers	PCL-MRW 3%	-59.13 ± 0.24	65.73 ± 0.59	95.13 ± 2.94	0.62	33.83 ± 0.37
	PCL-MRW 6%	-57.53 ± 0.34	66.39 ± 0.22	93.53 ± 0.47	0.63	34.35 ± 0.30
	PCL-MRW 9%	-57.36 ± 0.08	64.45 ± 1.30	89.04 ± 1.65	0.62	34.39 ± 0.06
	PCL-MRW 12%	-57.35 ± 0.19	65.26 ± 0.01	87.20 ± 2.76	0.63	33.11 ± 0.06

Figure 2: Typical stress-strain curves obtained from tensile tests for PCL-based nanocomposite films reinforced with 3 wt% modified Luffa cylindrica whiskers (○) and 3 wt% modified ramie whiskers (Δ). The behavior of the neat PCL matrix (■) is added as reference.

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Table 3: Mechanical properties of PCL films reinforced by either unmodified cellulose nanowhiskers or PCL- modified nanocrystals as determined by tensile testing: Young's modulus (E), stress (σ) and strain (ε) at break.

Filler	Sample	T_g (°C)	T_m (°C)	ΔH_m (J.g^{-1})	χ_c	T_c (°C)
	PCL matrix	-62.0 ± 0.23	63.4 ± 0.42	80.70 ± 0.85	0.51	22.8 ± 0.36
Unmodified Luffa Whiskers	PCL-ULW 3%	-59.19 ± 0.16	65.63 ± 0.01	84.29 ± 2.12	0.55	33.05 ± 0.16
	PCL-ULW 6%	-57.69 ± 1.62	65.29 ± 0.1.13	86.70 ± 1.49	0.58	33.67 ± 1.21
	PCL-ULW 9%	-57.41 ± 0.34	65.24 ± 0.30	80.24 ± 1.54	0.56	34.35 ± 0.84
	PCL-ULW 12%	-58.84 ± 1.17	66.09 ± 0.28	77.91 ± 2.06	0.56	35.70 ± 0.15
Modified Luffa Whiskers	PCL-MLW 3%	-59.03 ± 0.78	64.20 ± 1.21	95.29 ± 0.83	0.63	35.14 ± 0.07
	PCL-MLW 6%	-57.71 ± 0.25	64.17 ± 0.99	92.67 ± 1.33	0.63	35.08 ± 1.13
	PCL-MLW 9%	-58.01 ± 0.33	64.73 ± 0.16	88.90 ± 1.21	0.62	34.63 ± 0.25
	PCL-MLW 12%	-57.29 ± 0.33	64.90 ± 0.09	88.59 ± 2.89	0.64	35.06 ± 0.31
Unmodified Ramie Whiskers	PCL-URW 3%	-58.05 ± 0.23	64.67 ± 0.32	89.90 ± 3.35	0.59	34.16 ± 0.38
	PCL-URW 6%	-59.55 ± 0.33	64.76 ± 2.20	89.36 ± 1.49	0.61	33.25 ± 0.06
	PCL-URW 9%	-60.32 ± 1.09	65.58 ± 0.09	83.18 ± 2.79	0.58	33.79 ± 0.06
	PCL-URW 12%	-60.45 ± 1.24	65.90 ± 1.08	83.22 ± 1.51	0.60	34.37 ± 0.54
Modified Ramie Whiskers	PCL-MRW 3%	-59.13 ± 0.24	65.73 ± 0.59	95.13 ± 2.94	0.62	33.83 ± 0.37
	PCL-MRW 6%	-57.53 ± 0.34	66.39 ± 0.22	93.53 ± 0.47	0.63	34.35 ± 0.30
	PCL-MRW 9%	-57.36 ± 0.08	64.45 ± 1.30	89.04 ± 1.65	0.62	34.39 ± 0.06
	PCL-MRW 12%	-57.35 ± 0.19	65.26 ± 0.01	87.20 ± 2.76	0.63	33.11 ± 0.06

It can be observed that PCL matrix, as well known, is a quite ductile polymer at room temperature, able to undergo large deformations, however, it possesses relative low elastic modulus making it useless for any application where high rigidity is required. The addition of unmodified cellulose nanowhiskers, from *Luffa cylindrica* and ramie, up to 12 wt %, into PCL contributes to improve its Young's modulus. The other mechanical properties, specially the ultimate elongation, were drastically reduced as a consequence of filler aggregation. According to Habibi et al.(Habibi et al. 2008), zones with accentuated fragility are created in this kind of nanocomposites, which led to brittleness the composites. Actually there is lack of compatibility between the unmodified *Luffa cylindrica* and ramie nanowhiskers with PCL matrix. Therefore these results indicated there are very little or no effective stress-transfer properties.

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The addition of modified *Luffa cylindrica* and ramie nanowhiskers into PCL improved considerably the Young's modulus, which increases from 263 MPa for neat PCL to 393 MPa and 427 MPa for nanocomposites containing 12 wt% of ramie and *Luffa cylindrica* nanowhiskers, respectively. Higher aspect ratio of *Luffa cylindrica* nanowhiskers compared to Ramie nanowhiskers lead to higher improvement of Young's modulus. Moreover, regarding *Luffa cylindrica* whiskers, the chemical modification seems to allow better compatibility with the matrix. That's why *Luffa cylindrica*-nanocomposites (12 wt%) also presents higher elongation.

The results of DMA analyses have shown that the storage modulus of nanocomposites, especially chemical modified nanocomposites, increased upon filler addition, in agreement with tensile tests.

Conclusions

Morphological characteristics of *Luffa cylindrica* and ramie whiskers were successfully characterized by transmission electron microscopy (TEM). The surfaces of two different cellulosic nanowhiskers were chemically modified by grafting long chain isocyanate (N-octadecyl isocyanate - $C_{18}H_{37}NCO$). PCL-nanocomposites prepared with unmodified and modified nanowhiskers were characterized and demonstrated significant improvements in terms of mechanical properties, especially when modified nanowhiskers are used to reinforce PCL matrix. It was demonstrated that modified nanowhiskers have high potential applications in the field of bionanomaterials.

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