

Biodegradable polylactide/chitin composite fibers: processing, structure and mechanical properties

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Summary

Monofilament fibers based on Polylactide (PLA) and PLA filled with various chitin nanofibrils (CN) were processed by using a twin-screw extruder. Orientation of composite fibers was carried out.

The phase morphology of PLA-chitin composites was observed by scanning electronic microscopy. Rheological and thermal properties of composites were studied.

The influence of the CN types on the mechanical properties of oriented and non-oriented fibers was studied. The type of CN, which are most promising for obtaining a highly oriented fiber, was installed.

Riassunto

Sono state lavorate ed estruse fibre naturali formate da acido polilattico (PLA) e nanofibrille di chitina (CN) verificandone successivamente l'orientamento nel composito ottenuto. La relativa morfologia è stata verificata con la microscopia elettrica a scansione (SEM) studiando anche le proprietà reologiche e termiche dei compositi.

E' stata così controllata l'influenza esercitata da CN sulle proprietà e l'orientamento delle fibre.

In conclusione si è visto che CN è molto utile per ottenere un elevato orientamento delle fibre.

INTRODUCTION

Biodegradable polymers have increasing interest over the past two decades in the fundamental research as well as in the chemical industry. The practical value of biopolymers is determined first of all by their ability to biodegradability and biocompatibility. However, only a few types of polymers have been developed as candidates for medical applications, primarily because of their biocompatibility requirements. These polymers include, particularly, polylactide (PLA), polyglycolide (PGA) and their copolymers, poly(ϵ -caprolactone) or some natural polymers such as chitin, chitosan and collagen. Among these polymers PLA type polymers have been applied widely for medical application because of their good biocompatibility, biodegradability, high mechanical strength, and excellent processability by using melt technology. Within the state of current PLA research, many studies have been performed to synthesize PLA with controlled structure and properties. PLA can be easily processed by conventional processing techniques used for thermoplastics like injection moulding, blow moulding, thermoforming and extrusion (1).

A large number of investigations have been carried out on PLA and its copolymers in biomedical applications for resorbable medical implants in the shape of rod, plate, screw, fiber, sheet, rod, sponge, beads for bone and tissue engineering, microsphere for drug delivery system (2, 3). Optimal physico-mechanical properties and shorter degradation time of PLA and its copolymers are generally preferred in such pharmaceuticals applications.

One of the ways to improve mechanical and other physical characteristics is to incorporate some stiff filler phase into the polymer matrix. Often, it was pointed out that the reinforcing phases of the biopolymer is not biodegradable and biocompatible (4), thereby making such composite material medically unsuitable. There exist

several biopolymers from which biocompatible nanofillers can be created.

Chitin and chitosan offer a unique set of characteristics: biocompatibility, biodegradability to harmless products, nontoxicity, physiological inertness, antibacterial properties, heavy metal ions chelation, gel forming properties and hydrophilicity, and remarkable affinity to proteins (5). Owing to these characteristics, chitin- and chitosan-based materials, as yet underutilized, are predicted to be widely exploited in the near future especially in environmentally benign applications in systems applied in biological environments.

PLA composites and nanocomposites have been well studied in literature (6, 7), however little record exists for PLA-chitin nanocomposites (8). The existing literatures are largely only relevant to biomedical application dealing with solution blended chitosan-PLA composites (9-11). Thus the application of chitin nanofibrils (CN) for the purposes of mechanical and physical improvements utilizing scalable manufacturing processes is a very important area to explore (3,12,13). Composite materials based on PLA/CN can be of great interest as surgical suture materials, but research work in this area is relatively little.

The aim of this work was to create fibers based on PLA and different types of CN by melt technology. To study the influence of types of CN on the physical and mechanical properties of composite fibers. To process highly oriented fibers based on PLA and CN could be promising for future use as surgical suture materials.

MATERIALS AND METHODS

Materials

Matrix: Semi-crystalline Poly Lactic Acid (PLA), Sinobiom™ PL50, was supplied by Sinobiom, China. The density is 1.25 g/cm³.

Nanofillers: Chitin nanofibrils of three types (Mavi Sud s.r.l, Italy) were used.

- 1) Chitin nanofibrils (CN) was obtained by lyophilization of the initial chitin suspension. As a result, the powder consisting of the microparticles was obtained. Figure 1 represents the SEM micrographs of the material taken at different magnifications. It is evident that the microparticles have a strip morphology with the characteristic width of about 30 μm and the thickness of 0.1 μm (Fig.1a); they consist of nanofibrils with the width of 20 nm and the length in the range of 600–800 nm (Fig.1b).
- 2) Chitin nanoparticles-biolignin (CN-LG) was done adding slowly a 2% water solution of purified biolignin at pH 12(w/w) into a 2% water suspension of chitin nanofibrils(w/w) at pH 1.9.
After a mixing of 1 hour at a temperature of

50–60 °C, PEG is added slowly, mixing for a ~1 h. When at room temperature, the suspension was spray dried to obtained a dark brown powder consisting of the particles with a shape close to spherical. Modified nanoparticles have size in the range from 10 μm to 60 nm (Fig.2a).

- 3) Chitin nanoparticles modified with PEG (CN-PEG). was done at a 2% water suspension of CN (pH 1.9) neutralized at pH 7 by a 10% water solution of NaOH, is slowly added a 2% water solution of PEG at room temperature by a slowly mixing. Soon after the suspension is spray dried to obtain a light brown powder consisting of the spherical particles with diameter in the range from 10 μm to 67 nm (Fig.2b).

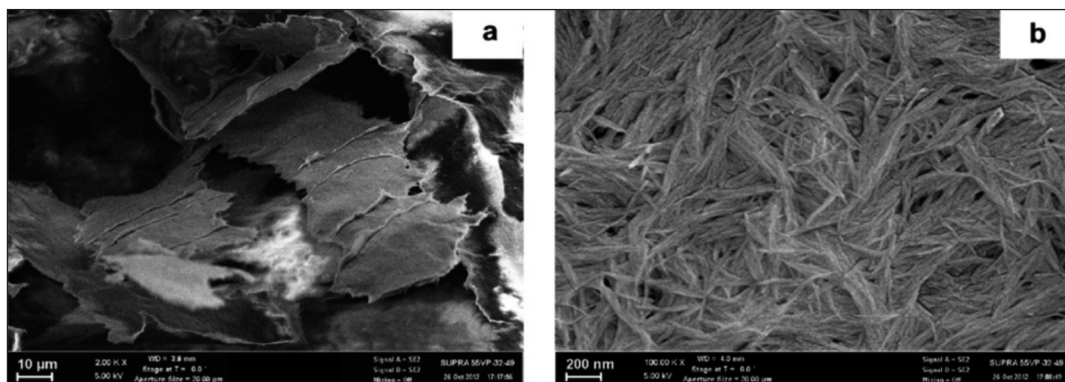


Fig. 1 Scanning electron micrographs of the film obtained from chitin nanofibril water dispersion by freeze drying (a and b).

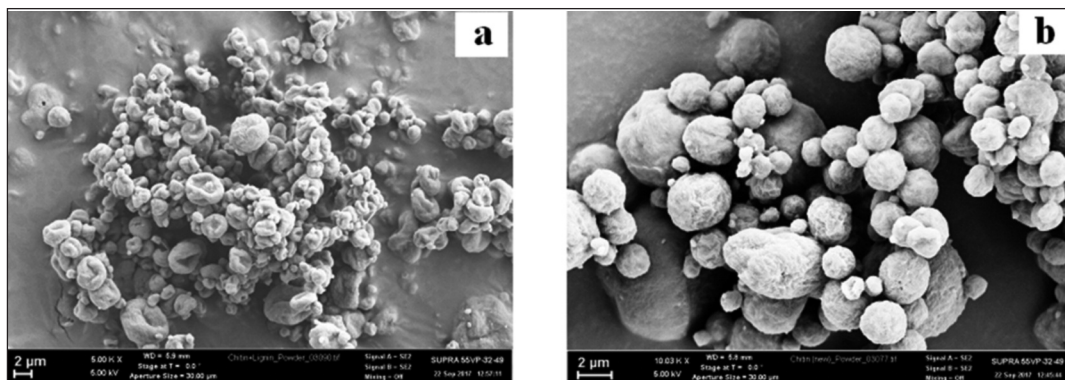


Fig. 2 Scanning electron micrographs of the powder of chitin nanoparticles modified with biolignin (a) and PEG (b).

Methods

Processing of nanocomposites

CN and oven-dried PLA were mixed on a 5 mL double-screw microextruder (DSM Xplore, Netherlands) at the screw rate of 50 min⁻¹ and temperature 220°C.

In order to minimize thermal degradation of both components, the mixing time was kept low as 5 min. At the exit of a Spinneret with a diameter of 1 mm after mixing, the melt was cooled with a jet of compressed air was supplied to the coil receiver placed at a distance of 260 mm from the extruder and rotating at a speed of 20 min⁻¹. As received monofilament was subjected to orientation drawing by four times ($\lambda = 4$) at the temperature 65±5°C with the use of special equipment. The resulting PLA-based composite in the form of non-oriented and oriented fibers were obtained.

Chromatography

The molecular weight (MM) characteristics of the polymers were determined by the method of liquid-liquid chromatography using a liquid chromatograph Prominence (Shimadzu) equipped with a refractometric (RID-10A, Shimadzu) detector. The HR 4E Styragel column, (Waters, 5 μ m, 7.8x300mm) was thermostated at 40 °C. THF was used as a mobile phase, the flow rate was 0.5 mL / min. Polystyrene standards (Agilent Technologies) were used to calibrate the column. THF was distilled over KOH and stabilized by adding 0.02% BHT.

Thermal methods

The thermal analysis of polymer was performed by the TGA and DSC methods. The TGA measurements were carried out on a Netzsch TG 209 F1 Iris analyzer (Germany) in an inert medium

in the temperature range of 30–600 °C at the heating rate of 10 K/min. The DSC analysis of copolymer was also performed in an inert medium on a Netzsch DSC 204 F1Phoenix analyzer (temperature range of –80 to +280 °C, heating rate of 10 K/min). The DSC method was used to determine the glass transition, crystallization and melting temperatures.

Rheological studies

Rheological behaviors of pure polymer and PLA-based composite were investigated by using a Physica MCR-301 rheometer (Anton Paar, Austria), with a cone-plane metering unit (25 mm in diameter, angle of 2°) All measurements were performed in shear mode at 220°C and a frequency of 0,1 s⁻¹. The temperature range of tests was chosen on the basis of the data of TGA and DSC.

Mechanical properties

The mechanical properties of PLA monofilaments prepared by melt spinning were studied on an Instron 5943 tensile test machine. The sample base length was 100 mm and the extension rate was 50 mm/min. From stress-strain diagrams of the samples, their strength σ_b , Young modulus E_0 and elongation at break ϵ_b , strength in a simple knot σ_{knot} were determined.

Microscopy

SEM images of the cryocleavage surface of PLA/CN monofilaments were recorded on a Carl Zeiss Supra-55 scanning electron microscope (Germany). All specimens were gold coated prior to observation.

RESULTS AND DISCUSSION

Molecular mass of PLA was estimated by using

chromatography method. Number average mass (M_n) of PL50 is 80 kDa and weight average mass (M_w) is 42 kDa, polydispersion $PD=1,76$.

The technological parameters of PLA processing were selected by using TGA, DSC and rheological analysis. Thermogravimetric and DSC curves is showed on figure 3. The temperature of beginning of weight loss of PL50 is 290°C (Fig. 3, curve I, point 1).

DSC curve (Fig.3, curve II) show glass transition temperature $T_g=70^\circ\text{C}$ (fig.1, point 2) and a distinct endothermic peak at 180°C (Fig.3, point 3) of PL50 can be attributed to the melting point (T_m) of the PLA crystallites (14, 15).

Chromatography and thermogravimetric analysis showed that PL50 is pure materials without impurities and suitable for processing by melt technology. Processing temperature of the polymer should be around 220 °C.

The stability of the rheological characteristics of the PLA melt in time in the atmospheric medium at this temperature were investigated (Fig.4, line 1). It is shown that viscosity decreases from 6500 to 1800 Pa·s during 30 minutes.

This imposes a limitation on the processing time of the PLA at least 10 minutes.

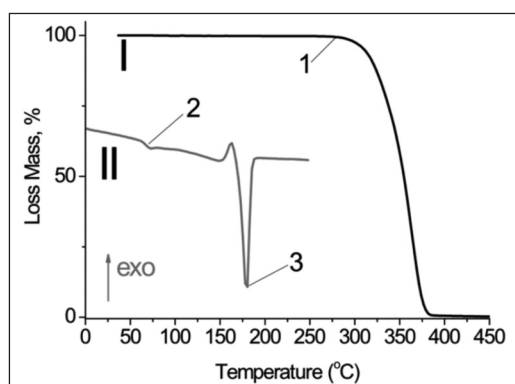


Fig. 3 Thermogravimetric (I) and DSC (II) curves of PL50: 1-temperature of beginning of weight loss; 2-the glass transition temperature; 3-melting temperature.

Further melt spinning of PLA composite monofilaments was processed on a twin-screw micro-

extruder with regard to the set technology parameters of material processing.

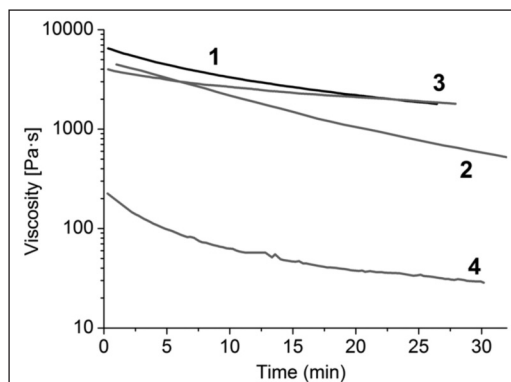


Fig. 4 Dependence of viscosity of pure polymer and PLA-based composite on time at the 220 °C: 1 - pure PLA; 2 - PLA+1%CN-PEG; 3 - PLA+1%CN; 4 - PLA+1%CN-LG.

Structures of PLA-chitin composites

To investigate the phase morphology of PLA/CN blends, fractured surfaces at room temperature of the blends were observed by SEM after being gold coated. As shown in figure 5, chitin particles of all three types are evenly distributed in the PLA matrix and retain their original dimensions and shape. But in the case of CN, some particles are combined into conglomerates with size up to 20 μm . As seen, it was not possible to achieve dispersion to the nanoscale level of the part of CN.

Thermal properties of PLA-chitin composites

TGA curves for different types of chitin were carried out to evaluate their degradation profiles and thermal stability (Fig. 6.). In the thermogram of CN-PEG, there was one degradation step, which starts at $\tau_s=335^\circ\text{C}$, determined by the derivative TGA curves. TGA curve for CN sho-

wed the start thermal degradation nanofiller at $\tau_s=250$ °C. CN-LG showed a combination of thermal degradation of lignin and chitin at the temperature of 210 and 340 °C respectively [16, 17]. As mentioned above, the processing temperature of the composites is 220 degrees, which

can lead to the destruction of the filler, as well as to the destruction of the polymer matrix. Also it is seen (Fig. 6) the mass losses for CN-LG and CN at the temperature of $\tau_i=100$ °C. Thus, these fillers must be dried before mixing with PLA with used the extruder for removing of water.

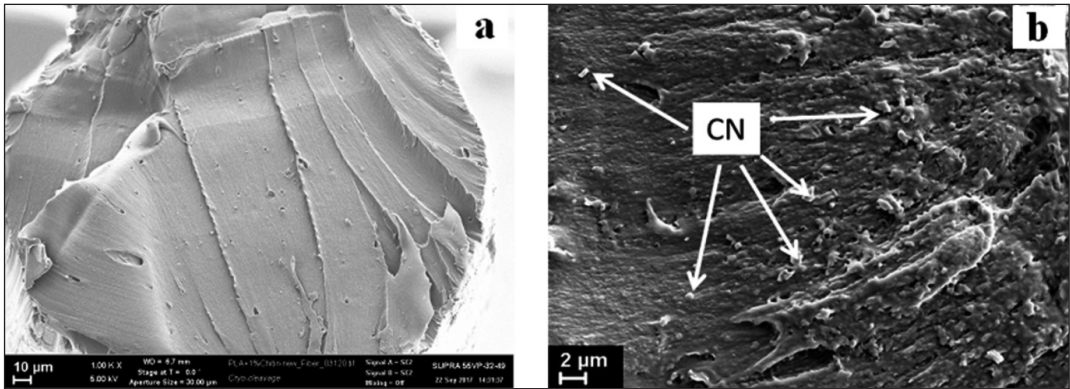


Fig. 5 Micrograph of fractured surface of PLA+1%CN.

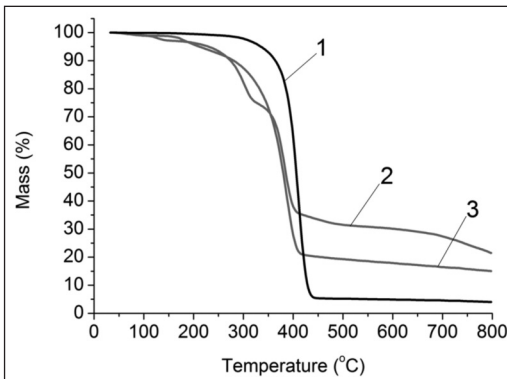


Fig. 6 Thermogravimetric curves of different types of chitin: 1 – CN-PEG; 2 – CN-LG; 3- CN.

DSC scans were performed for three PLA/CN composites are presented in figures 7 and 8. The results (Fig.7) indicated that CN and CN-PEG does not significantly influence on the glass transition and melting behavior of PLA, which were at 62°C and 180°C. But PLA/CN-LG blend has double melting peaks at temperature 160 and 168 °C. Fig. 8 illustrates that chitin in any form except for chitin, modified lignin,

can serve as a crystal nucleating interface, increasing the crystallinity from 8,6 J/g for pure PLA to the 11,8 and 37,9 J/g for PLA filled with CN-PEG and CN, respectively (18). In addition, only the CN content has influence on the crystallization temperature which is slightly increased up to 105°C, while for the pure PLA it is 96°C (Fig. 8, line 1).

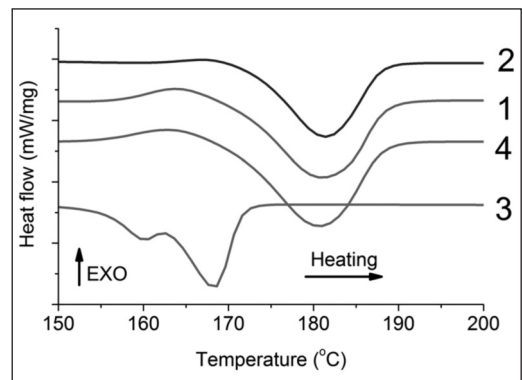


Fig. 7 DSC curves of PLA/Chit composites (2 scan): 1 – pure PLA; 2 – PLA+1%CN; 3 - PLA+1%CN-LG; 4 - PLA+1%CN-PEG.

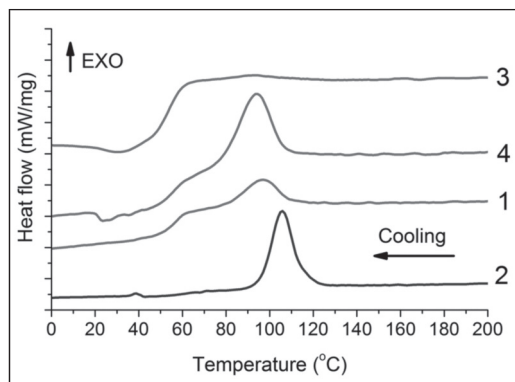


Fig. 8 DSC curves of PLA/Chit composites (cooling): 1 – pure PLA; 2 – PLA+1%CN; 3 – PLA+1%CN-LG; 4 – PLA+1% CN-PEG.

Rheological behaviors of PLA-chitin composites

According to the results of rheological analysis (Fig. 4) it can be noted that a melt of PLA with CN-LG has the lowest viscosity of about 200 Pa·s compared to other composites. It decreases in the course of the experiment due, probably, to destruction of the CN-LG particles during its dispersion in the polymer melt at temperature of 220°C (see TGA curves of chitin fillers (Fig.6). This destruction of CN-LG can decrease molecular weight of PLA in turn.

The incorporation of CN and CN-PEG into PLA do not increase the melt viscosity of the compo-

sites and their viscosities are about 4000 Pa·s. It should be noted that the viscosity of PLA filled with CN-PEG is reduced over time, and filled with CN is almost stable. Viscosity of PLA filled with CN-PEG decreases up to 400 Pa·s during 30 min of test, while viscosity of PLA-CN decreases only up to two times ($\eta=1800$ Pa·s).

It is known that if the dispersion of the filler to the nano-sized particles is the sharp increase of melt viscosity at low shear rates, the reason for this is the formation of a structure (percolation) in the grid of nanoparticles in the volume of the polymer matrix. In this case, the chitin fibrils likely failed to destroy up to nanoscale level. Further work will be carried out to improve the technology of dispersion chitin nanoparticles in the melt PLA.

Tensile properties of PLA-chitin composites

The results of mechanical tests of the non-oriented PLA/CN composites are presented in Table I. As can be noted from Table I particles CN in the quantity of 1% do not influence practically on the mechanical properties of the composite fibers and all mechanical parameters remain at the level of pure PLA taking into account the error: tensile strength ~ 50 MPa, Young modulus ~ 2.6 GPa, and elongation at the break remains at the level of 100%.

TABLE I				
Mechanical properties of non-oriented PLA-chitin nanofibrils composites				
Parameter	PLA	PLA+1% CN	PLA+1%CN- LG	PLA+1%CN- PEG
Tensile Strength, MPa	55±10	45±8	65±17	36±1
Young modulus, GPa	2,6±0,1	2,6±0,2	4,0±0,2	3,0±0,1
Elongation at the break, %	100±50	80±60	3,1±0,8	1,6±0,2

Fibers with the addition of CN-LG have a strength slightly higher than CN ($\sigma_b=65$ MPa), but they are brittle with deformation up to a break of 3%. Young modulus of this composites is higher than pure PLA ($E_0=4$ GPa). At the same time monofilaments with CN-PEG has also brittle deformation up to a break of 1%. The strength of these monofilaments is lower than that of the initial 36 MPa.

The elastic modulus is slightly higher than pure PLA ($E_0=3$ GPa). Thus, the introduction of CN-LG and CN-PEG leads to the embrittlement of PLA fibers. Only composites with CN are suitable for further high-temperature orientational draw by 4 times ($\lambda=4$).

Mechanical properties of oriented fibers based on pure PLA and PLA+1%CN are shown on Figure 9 and in Table 2.

Figure 6 shows representative stress–strain curves for oriented PLA and PLA–CN fibers containing 1% Chit. It can be noted (table 2) that the addition of 1% CN nanoparticles reduces the strength of composites fibers compared with pure PLA. So the strength of PLA+1%CN is 246 MPa, while pure PLA have $\sigma_b = 274$ MPa. It can be seen that at 1% CN, The Young modulus of the composites and elongation at the break slightly decrease (table II).

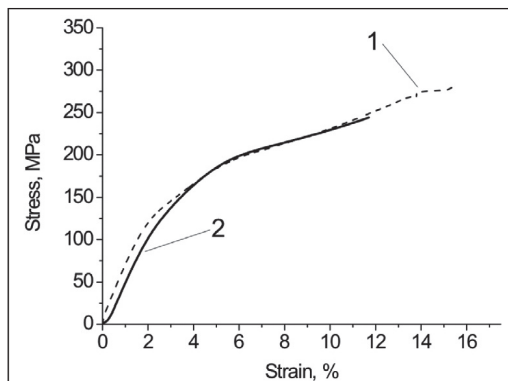


Fig. 9 Stress–strain curves of oriented fibers based on PLA (1) and PLA+1%CN (2).

The data values of the filler concentration is likely to impede the realization of the orientation process in the polymer matrix and reduce the likelihood of the formation of structures responsible for the mechanical properties of the material, which leads to a drop in the strength of composite fibers.

Composite fibers based on polylactide with chitin can be used as suture surgical materials. Strength in the knot is one of the indicators of quality material of suture yarns.

TABLE II

Mechanical properties of oriented fibers based on pure PLA and PLA+1%CN.

Parameter	PLA	PLA+1% CN
Tensile Strength, MPa	276±20	246±4
Young modulus, GPa	6,2±0,3	5,7±0,1
Elongation at the break, %	16±4	12±1
Strength in a simple knot, MPa	168±40	179±26

Comparison of the strength in the knot of oriented fibers based on pure PLA and filled with 1% CN is presented in table 2 also. It is seen, the strength of the fibers in the knot decreases in the comparison with the tensile strength by 40 and 30%, respectively, for pure PLA and PLA/CN. The introduction of chitin fibrils does not lead to a decrease in the strength in the knot, which remains at the level of a pure PLA. The spread of values is within the measurement error. Such a result is extremely important in the development of surgical composite materials (fibers, yarns), the level of mechanical properties of which is primarily estimated by the strength of the knot.

CONCLUSION

As a result of the work, composite materials were obtained in the form of fibers based on PLA and various chitin particles (CN, CN-PEG and CN-LG) in the concentration 1wt%.

The phase morphology of PLA–chitin composites was observed by scanning electronic microscopy (SEM). Nanoparticles are uniformly distributed in the PLA matrix, but some particles united in conglomerates the size of 20 μm . It should be noted that the viscosity of PLA filled with CN is almost stable at the time compared with pure PLA and other composites.

The addition of chitin particles modified by lignin leads to the degradation of the PLA during processing by melt technology. Addition of CN and CN-PEG particles to a polymer induces heterogeneous crystal nucleation resulting in increased crystallinity.

The influence of the type of chitin particles on the mechanical properties of oriented and non-oriented fibers were studied. It is shown that introduction of 1% CN-LG and CN-PEG make the composites fibers brittle, while mechanical characteristics of non-oriented fibers PLA filled with chitin remain at the level of pure PLA.

Promising composite fiber PLA+CN are suitable

to orientational draw. Such high oriented fibers may be promising for the development of surgical suture materials with regulated physical and mechanical properties.

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References

- 1) Gupta AP, Vimal K. (2007) New emerging trends in synthetic biodegradable polymers–Polylactide: A critique. *Eur. Polymer J.*, **43**:4053–4074.
- 2) Chen Y, Geever LM, Killion JA, Lyons JG, Higginbotham CL. (2016) Review of Multifarious Applications of Poly (Lactic Acid). *Polymer-Plastics Technol. Engin.*, **55**(10):1057–1075.
- 3) Dobrovolskaya IP, Yudin VE, Popryadukhin PV, Ivan'kova EM. (2016) Polymer matrixes for tissue engineering. St.-Petersburg, p.224 (in Russian)
- 4) Dean K, Li L, Yu L. (2006) Polymer blends and composites from renewable sources. *Prog. Polym. Sci.*, **6**(31):576–602.
- 5) Krajewska B. (2004) Application of chitin- and chitosan-based materials for enzyme immobilizations: a review. *Enz. Microb. Technol.*, **35**(25):126–139.
- 6) Bertioz S, Chailan J-F, Panaitescu DM, Donescu D, Frone AN. (2011) Cellulose fiber-reinforced polylactic acid. *Polym. Compos.*, **32**(6):977–985.
- 7) Mathew AP, Bondeson D, Kvien I, Oksman K. (2006) Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. *Compos. Sci. Technol.*, **66**(15):2776–2784.
- 8) Reza R, Cochrane B, Naguib H, Lee PC. (2011) Fabrication and characterization of melt-blended polylactide-chitin composites and their foams. *J. Cell Plast.*, **47**(3):283–300.
- 9) Balcerzak J, Mucha M. (2010) Analysis of model drug release kinetics from complex matrices of polylactide-chitosan. *Progr. Chem. Appl. Chit.*, **15**:117–125.
- 10) Lenos AF, Ferreria JMF, Araujo ABA. (2009) Rheological, microstructural and vitro characterization of hybrid chitosan-polylactic acid/hydroxyapatite composites. *J. Biomed. Mater. Res.*, **4**(88):916–922.
- 11) Wu Q, Wang S, Zhang S, Hu Z, Wan Y. (2007) Mechanical properties of porous polylactide/chitosan blend Membranes. *Macromol. Mater. Eng.*, **5**(292):598–607.
- 12) Volova TG. (2009) Materials for medicine, cells and tissue engineering. Krasnoyarsk: 116. (in Russian).
- 13) Ramakrishna S, Mayer J, Wintermartel E, Kam WL. (2001) Biomedical applications of polymer-composite materials: A review. *Comp. Sci. Technol.*, **61**:1189–1224.
- 14) Signori F. (2009) Thermal degradation of poly(lactic acid) (PLA) and poly(butylenes adipate-co-terephthalate) (PBAT) and their blends upon melt processing. *Polym. Degrad. Stability*, **94**:74–82.
- 15) Lim LT, Auras R, Rubino M. (2008) Processing technologies for poly(lactic acid). *Prog. Polym. Sci.*, **33**(8):820–852.
- 16) Hui Zhou, Yan Qiu Long, Ai Hong Meng, Qing Hai Li, Yan Guo Zhang (2013) The pyrolysis simulation of five biomass species by hemi-cellulose, cellulose and lignin based on thermogravimetric curves. *Thermochimica Acta*, **566**(20):36–43.
- 17) Tang Wanjun, Wang Cunxin, Chen Donghua (2005) Kinetic studies on the pyrolysis of chitin and chitosan. *Polym. Degrad. Stability*, **87**(3):389–394.

- 18) Rizvi R, Cochrane B, Naguib H. and Lee PC. (2011)** Fabrication and characterization of melt-blended polylactide-chitin composites and their foams. *J. Cell. Plast.*, **47(3)**:283-300.

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