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The Preparation and Characterization of Melt-spun PLA Multi-filament Modified with Myrrh Extract†

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Abstract: Using the melt spinning process, various multifilaments can be formatted from different polymers or their complex. Polylactide (PLA) is one of the most widely used synthetic biopolymers obtained from renewable resources. The biggest advantages of PLA over petroleum-based polymers is that they are biodegradable and biocompatible. Myrrh resin is known for a long time as a good antimicrobial and antifungal material. In this study, multifilament yarns from modified biodegradable PLA granules with the highest ethanolic myrrh extracts were developed and characterized. The results showed that it is possible to form PLA melt-spun multifilament yarns with 10% myrrh extract. The mechanical properties of PLA melt-spun multifilament yarns formed from PLA granules ethanolic extract, respectively. It was estimated that melt spun multifilament yarns from PLA with myrrh extract have higher linear density, lower breaking force, and higher elongation at break compared with pure PLA multifilament yarns. The increase of draw ratio causes the decrease of multifilament yarn linear density, decreases breaking force and increases elongation at break.

Keywords: Myrrh, PLA, melt spinning, multifilaments yarns

1. Introduction

Textiles are an integral part of various medical applications including non-implantable, implantable materials, healthcare products. Existed are many medical manufactured technologies such as weaving, knitting, braiding, nonwoven, and various spinning technologies. One of the possible ways to form medical textiles can be melt spinning. Despite the fact that in this process no solvent is needed, this process stands out his simplicity of the production line, high spinning velocities, low production cost. In the process of melt spinning, it is possible to use additives and form multicomponent yarns with various functionalities. The yarns formed in this way are ideal for use in the field of medicine [1,2].

Polylactide (PLA) is synthesized from natural resources (most often from corn). He has several of bio-properties, e.g. good biocompatibility, biodegradability by enzyme and hydrolysis under physiological conditions, and antibacterial activity, which are suitable for biomedical use [3]. Also PLA is the only biobased and biodegradable polymer which can be large-scale melt-spun to textile fibers with sufficient strength [4].

As mentioned above, different active biocides, such as antimicrobial, fungicidal, or antifouling agents, are incorporated into textile materials and their surfaces to make them bioactive. The most commonly used are metals and metallic salts such as silver, copper, and zinc [5]. The potential hazards to human and environmental health of these antimicrobial agents are a critical ongoing research topic, both during the production, use, and

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end life of textile materials [6]. Natural components could be a solution to healthier, profitable and sustainable additives in functional antimicrobial fiber [7].

Commiphora myrrha (Myrrh) resin is obtained from a small tree, especially occurring in northeastern Africa, southern Arabia, and India [8]. Myrrh consists of alcohol-soluble resins (25–40%), volatile oils (3–8%), and water-soluble gum (30– 60%); containing polysaccharides, proteins, and long-chain aliphatic derivatives [9]. Myrrh has a range of applications and benefits, e.g., in the treatment of anti-inflammatory diseases and many infectious diseases, and it is becoming a very popular and valuable alternative medicine. Its extracts have been used to cure wounds, ulcers, and different diseases of the respiratory, gastrointestinal and urinary tract [10].

The aim of this research is to investigate the possibilities of forming biodegradable melt-spun multifilament PLA yarns with 10% myrrh resin. In this research, the influence of myrrh extract on the mechanical properties of PLA melt-spun yarns was investigated.

2. Materials and Methods

2.1. Materials

Polylactic acid (PLA) Polymer 6202D (Nature Works, Blair, NE, USA) was used as the main material for multifilament yarns. This thermoplastic has a density of 1.24 g/cm^3, a crystalline melt temperature of 155-170 ° C and a glass transition temperature of 55-60 ° C. [11]. Myrrh resin was imported from India (Ekokolekcija, Vilnius, Lithuania). Agricultural origin ethanol (96%) for solution was purchased from the company 'Stumbras' (Kaunas, Lithuania).

2.2. Preparation of Myrrh Ethanolic Extract

Before the extraction process, solid particles of myrrh resin were crushed to a fine powder. The mass ratio of the myrrh rosin powder and the 96% ethanol extraction mixture was 30/70. The myrrh ethanolic extract was produced for 12 h in a round bottom flask at the boiling point of ethanol (approximately at 78 °C). The mixture was stirred with a magnetic stirrer at 400 rpm (IKA RH, basic KT/C, Staufen, Germany) throughout the extraction period. Reflux condenser (Allihn type, Schott AG, Mainz, Germany) was used to prevent solvent evaporation from the boiled ethanolic myrrh extract. The ethanolic extract of myrrh was filtered using Filtrak No. 389 filter paper using a Buchner funnel to remove the undissolved solid particles (the sand and ethanol-insoluble part of myrrh).

2.3. Modification of PLA Granules with Myrrh Extracts

PLA granules were modified with myrrh ethanolic extract by the spraying process. The PLA granules were covered with myrrh extracts, mixed and dried at a temperature of 80 °C for at least 60 min until the solvent ethanol had evaporated. The coating step was repeated four times, while bicomponent PLA/Myrrh extract granules of 90/10 wt/wt were formed.

2.4. Melt Spinning of PLA Multifilament Yarns

Multifilament yarns from PLA polymer and PLA modified with myrrh ethanolic extract, manufactured by COLLIN® CMF 100 single screw extruder equipment (Dr. Collin Gmbh, Germany). The single screw extruder (L/D = 25:1) has seven heating zones, where the temperature during the experiments was set at 220 ° C. The average speed of the extruder was set to 29 rpm. Circular spinnerets (Figure 1 indicated by SP) with 24 holes (diameter 0.45 mm) were used during these experiments. The cooling of the filaments (Figure 1 indicated by A) was achieved with cross-flow air quenching at a temperature of 15 ° C. The temperature of all stretching rolls was the same: S1 - S4 = 75 ° C.

Multifilament yarns from the polymers were formed by changing melt-spinning parameters. The conditions of yarn formation are given in Table 1

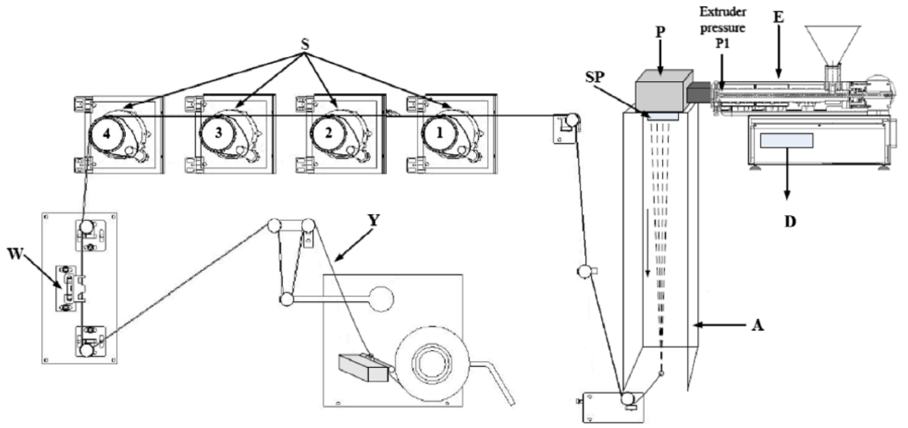

Figure 1. Principal scheme of the laboratory spinning equipment COLLIN ® CMF 100 (Dr. Collin Gmbh, Germany): E- extruder, P – melting pump, SP – spinneret, A – air quench cabinet, D – display, S – stretching gadgets, W – whirling unit, Y – multifilament yarn from microfibers [12].

Table 1. Parameters for spinning step to obtain multifilament yarns.

Code	**Samples**	**Stretching rolls speed m/min**				**Drawing ratio**
		S1	S2	S3	S4	
A	PLA	100	116	139	150	1.5
B	PLA with myrrh					
C	PLA	100	134	169	201	2
D	PLA with myrrh					
E	PLA	100	150	204	251	2.5
F	PLA with myrrh					
G	PLA	100	168	237	301	3
H	PLA with myrrh					

2.5. Linear Density of Yarns

Before the test, all multifilament samples were conditioned not less than 24 hours in the standard atmosphere according to the standard, that is, at a relative humidity of (φ = 65 % ± 4 % and a temperature of 20°C ± 2 ° C. Samples of 50 m in length were prepared by reeling skeins with Zweigle L232 (Zweigle Textilprüfmaschinen GmbH & Co. KG, Germany), for the estimation of the linear density of multifilament yarns. The mass of the skeins was determined under standard atmospheric conditions. The linear density of multifilament yarns was calculated according to the equation:

$$T=m/l, \tag{1}$$

tex where m – mass, g and l – length, km of a 50 m specimen.

The test result was calculated as an average of five measurements.

2.5. Mechanical Properties of PLA Multifilament yarns

The mechanical properties (breaking force and elongation at break) of the PLA multifilament yarns were determined according to the EN ISO 2062:2009 standard. The experiments were carried out in a standard atmosphere where the temperature was 20 ± 2 °C and the relative humidity was 65 ± 4%. Universal testing equipment Zwick/Roell (Zwick GmbH & Co. KG, Germany) with the testXpert® operating program was used. The length between the clamps was 250 mm and the stretching speed was 500 mm/min and a pretension of 0.5 cN/tex. The number of tensile tests for the package was 35.

3. Results and Discussion

3.1 The Influence of Myrrh Extract on the Structure and Mechanical Properties of Melt Spun PLA Multifilament Yarns

Table 2. Mechanical properties of formed multifilament yarns

Code of sample	Composition of sample	Linear density of multi-filament yarns (tex)	Breaking force (cN)	Strain at break (%)
A	PLA	81.7 ± 1.5	253 ± 21	75.5 ±4
B	PLA with myrrh	94.3 ± 1.3	239 ± 14	85 ± 3
C	PLA	76.1 ± 1.8	280 ± 19	45.8 ± 3
D	PLA with myrrh	78.1 ± 1.9	249 ± 15	58 ± 4
E	PLA	58.6 ± 1.1	292 ± 23	32.2 ± 2
F	PLA with myrrh	59.6 ± 0.8	246 ± 26	45 ± 4
G	PLA	46.3 ±1.9	297 ± 17	12.2 ± 1.5
H	PLA with myrrh	50.8 ± 2.5	257 ± 15	16 ± 3

The two main challenges of PLA granule modification with myrrh ethanolic extract. First, PLA granules are hydrofhobic, so to cover them requires time. Second, it is tricky to find the ethanolic myrrh concentratation which can be used to cover PLA granules. Because if the concentration is too high, the multifilament yarns do not form. Excessive concentration of myrrh extract can increase the melting phase separation of polymer complexes [13].

The linear density (tex) of multifilament yarns depends on technological parameters (melting temperature, drawing, pressure, and winding) and raw material [14,15]. From the results presented in Table 2, it is possible to notice that the linear density of melt spun yarns from pure PLA and PLA modified ethanolic myrrh extract depend on the technological parameters. Increasing the drawing ratio from 1.5 to 3 resulted in a linear density of pure PLA yarns decreasing approximately 43%, and modified PLA – 46%. The presence of myrrh extract had no significant effect on the linear density of melt-spun PLA yarns.

Tensile tests on melt spun pure PLA yarns and modified with ethanolic myrrh extract were estimated to determine how the mechanical properties yarns were influenced by the presence of myrrh extract. Comparing the mechanical properties of pure PLA multifilament and PLA multifilament with myrrh extract , it was observed that increasing drawing ratio breaking force increasing, but elangation at the break decreasing. The breaking force (f_f, cN) of A and B multifilament decreases, approximately 6%, but then the drawing ratio is higher (G and H samples), the breaking force decreases by approximately 16%. Estimated Students *t*-test values $t_{f\ A\text{-}B,\ cN}$= 4.7; $t_{f\ C\text{-}D,\ cN}$= 10.8 $t_{f\ E\text{-}F,\ cN}$= 11.2; $t_{f\ G\text{-}H,\ cN}$= 14.8 show that modification of PLA granules with myrrh extract have significant influence on multifilament yarns breaking force. Meanwhile, comparing strain at break (%), when drawing ratio increases, strain decreases. Estimated Students *t*-test values $t_{\varepsilon\ A\text{-}B\ \%}$ = 16; $t_{\varepsilon\ C\text{-}}$

$_{D\ \%}$ = 20; $t_{\varepsilon\ E\text{-}F\ \%}$ =24; $t_{\varepsilon\ G\text{-}H\ \%}$ = 9.6 show that modification of PLA granules with myrrh extract have significant influence on multifilament yarns strain at break.The tensile properties of multifilament yarns depends on the internal structure of the fibers and the different spinning conditions influence it [16]. Increasing drawing ratio contributed to better PLA polymer chain orientation, so breaking force increasing and strain at break decrease. After PLA modification with ethanolic myrrh extract breaking force a lower than pure PLA and strain at break a higher. The Myrrh resin in the PLA polymer matrix decreases in the mobility of the polymer chains of PLA, so breaking force is lower than that of pure PLA multifilament.

3. Conclusion

It was estimated that it is possible to melt spun multifilament yarns with high-content natural myrrh extract. The addition of the highest myrrh ethanolic extract (10%) to multifilament yarns didn't have a significant influence on linear density. The modification of PLA granules with ethanolic myrrh extract did not influence PLA melt flow, linear density, breaking tenacity, or the degree of crystallinity of melt spun yarns, though it did cause an increase in the elongation at break of yarns.

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