The centrifugal spinning of vitamin doped natural gum fibers for skin regeneration

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ABSTRACT

The study investigates the use of fiber carriers, based on biopolymeric gums as potential candidates for cosmetic and dermatological applications, in particular for skin regeneration. Gum arabic (GA), xanthan gum (XA), and gum karaya (GK) were used as the main gum materials for the fibers, which were prepared by centrifugal spinning from an aqueous solution. These solutions of different mass gum ratios were blended with poly (ethylene oxide) (PEO) for better spinnability. Finally, vitamins E and C were added to selected solutions of gums. The resulting fibers were extensively investigated. The morphology and structure of all fibers were investigated by scanning electron microscopy and Fourier transformed infrared spectroscopy. Most importantly, they were characterized by the release of vitamin E loaded in the fibers using UV-VIS spectroscopy. The presentation will show that the newly prepared fibers from GA and PEO represent a very promising material for cosmetic and dermatologic applications.

1. Introduction

In the last decades, an increasing interest in the use of biopolymers in various fields, especially in biomedical applications, has been observed. In particular, natural gums (such as gums arabic, karaya, xanthan, tragacanth, and chitosan) have attracted significant attention among various biopolymers, due to their unique and valuable properties such as biodegradability, biocompatibility and low-costs. These gums offer their potential for exciting applications in food industry, biomedicine, pharmaceuticals, etc. (Bhosale, Osmani, & Moin, 2014–2015; Goswami & Naik, 2014; Mukherjee, Sarkar, & Moulik, 2010; Poštulková, Nedomová, Hearnden, Holland, & Vojtová, 2019). There are several possible classifications of natural gums, but the most common one is their classification based on their origin. A relatively large group consisting of gum exudative (gum arabic, ghatti, karaya, tragacanth, khaya, and albizia) is obtained after removal from the corresponding wood (Goswami & Naik, 2014; Jania, Shahb, Prajapatia, & Jain, 2009).

Fiber materials (including especially nanofibers with a diameter on the nanoscale) are widely used for their attractive properties like high surface area, high porosity, breathability, tunable dimensions, mechanical properties, etc. Compared to other material's morphologies, the significant advantage of nanofibers is their ability to be produced from a wide range of natural and synthetic polymers, metals and metal oxides, carbon-based, and composite nanomaterials (Huang, Zhang, Kotaki, & Ramakrishna, 2003; Pavliňáková, Fohlerová, Pavliňák, Khunová, & Vojtová, 2018; Ramakrishna, Fujihara, Teo, Lim, & Ma, 2005). Although electrospinning has been so far the most common technique for preparing nanofibers on the laboratory scale, this technology has limitations. For example, it utilizes a very high electric field within highly flammable and often toxic solvents, it has an overall low production rate, and high solvent consumption (Ramakrishna et al., 2005; Barhate & Ramakrishna, 2007; McEachin & Lozano, 2012; Lu et al., 2013). On the contrary, centrifugal spinning is a very modern and industrially robust technique that overcomes the limitations of electrospinning. The most important parameters for centrifugal spinning include centrifugal force, the solution viscosity (given by polymer concentration), diameter of the nozzle, temperature and relative humidity, and distance of the collector. Depending on these parameters, a fiber diameter of several hundred nm to several μm can be achieved (Hromádko, Koudelková, Bulánek, & Macak, 2017; Rihova et al., 2021;

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Weitz, Harnau, Rauschenbach, Burghard, & Kern, 2008; Zhang & Lu, 2014).

Several studies have described preparations of electrospun fibers from natural gums. For example, the pure electrospun fibers were prepared from chitosan (Ohkawa, Cha, Kim, Nishida, & Yamamoto, 2004), dextran (Jiang, Fang, Hsiao, Chu, & Chen, 2004), cellulose (Kang, Choi, Kim, Song, & Kim, 2015; Viswanathan et al., 2006), xanthan gum (Shekarforoush, Faralli, Ndoni, Mendes, & Chronakis, 2017), and guar gum (Lubamboa et al., 2013; Yang et al., 2019). However, these fibers were prepared from solutions containing toxic organic solvents (e.g. *N, N,*-dimethylformamide dimethyl sulfoxide, formic acid) and had a very poor quality. Stijnman, Bodnar, and Tromp (2011) examined the prepared pure natural fibers by natural electrospinning. They showed that it is rather difficult to spin natural gums (without any additives) when the low-shear viscosity is low or high with a strong shear thinning. Overall, the preparation of fibers consisting of pure gums is limited, as described above. However, it is possible to prepare mixed fibers from solutions that contain gum(s) and suitable additives (such as synthetic polymers) and solvents.

In fact, fibers based on gums blended with other polymers can be shaped and modified according to the targeted application. In principle, these fibers could be prepared from various gums (gum arabic, karaya, tragacanth, xanthan, chitosan, potato starch, etc.), blends with other synthetic polymers, such as poly(ethylene oxide, poly(vinyl alcohol), poly(ε-caprolactone), etc. (Dror et al., 2003; Ohkawa et al., 2004; Padil & Černík, 2013; Padil, Senanb, Wacławek, & Černík, 2016; Rad, Mokhtari, & Abbasi, 2019; Ranjbar-Mohammadi, Bahrami, & Joghataei, 2013; Šukytė, Adomavičiūtė, & Milašius, 2010). Recently, new approaches to the use of polymeric fibers have also shown potential for cosmetic and dermatological applications. In general, different types of creams, hydrogels and films are often used for daily skin care and treatment of damaged skin (Martin & Glaser, 2011; Yilmaz, Celep & Tetik, 2016), and can often be limited by their application, e.g. due to easy contamination over time and prevention of skin ventilation (Dao et al., 2018; Kaul, Gulati, Verma, Mukherjee, & Nagaich, 2018). Some reports have already shown the preparation of electrospun fibers from various polymers with additives (vitamins, nanoparticles, fatty oil, etc.) for cosmetic and dermatologic applications. The vitamins (A, B, and C) are the most commonly used additives for facial skin care products and cosmetics due to their positive effects on the skin such as hydration, reduction of wrinkles and visible pores, etc. It is also well known that even a small addition of vitamins has positive effects on improving skin appearance. For example, Fathi-Azarbayjani, Qun, Chan, and Chan (2010) showed that fibers from poly(vinyl alcohol), ascorbic acid, retinoic acid, collagen, and gold have a positive effect on the skin surface due to the high surface area of the fibers. Sheng et al. (2013) have presented silk fibroin nanofibers loaded with vitamin E. Their findings showed that the prepared material has an enhancing effect on the proliferation of skin fibroblasts and improves the survival of the cells against oxidative stress. Taepaiboon, Rungsardthong, and Supaphol (2007) synthesized cellulose acetate fiber carriers for vitamin E and vitamin A. Miletić, Pavlić, Ristić, Zeković, and Pilić (2019) reported that the addition of fatty oil in fiber materials has antioxidant properties and high potential to be used in the cosmetic industry.

Moreover, a positive effect of vitamins was observed for the treatment of various dermatologic diseases, such as acne vulgaris, photodamage, and disorders of keratinization including psoriasis (Shapiro & Saliou, 2001). Vitamin E (tocopherol) is the major lipid-soluble antioxidant that is important for protecting skin cells from free radicals, thus protecting human skin from sunburn, reducing wrinkles, and hyperpigmentation of human skin. In addition, this vitamin is also used to treat almost various types of skin lesions and is often used to treat burns, surgical scars, and other wounds. The chemical structure of vitamin E includes a group of four tocopherols (α-, β-, γ-, and δ-T) and four tocotrienols (α-, β-, γ-, and δ-T3). Chemically, α-tocopherol is known as a powerful antioxidant due to the presence of hydroxyl group attached to

the aromatic ring, which can easily react with peroxyl radicals and thus protect the skin from the larger breakdown of skin collagen. Antioxidant supplementation of vitamin E together with synergistically active antioxidants, such as vitamin C may lead to an increase in the photoprotective effects of vitamin E (Baumann & Spencer, 1999; Thiele, Hsieh, & Ekanayake-Mudiyanselage, 2005; Nimse & Pal, 2015; Cassano, 2012).

All of the nanofiber literature given above utilizes electrospinning as the spinning technique of choice. However, the centrifugal spinning process has recently become a much more attractive technology for fiber production, as it has a higher production rate and overall it is easier to upscale, compared with electrospinning (Rihova et al., 2021; Zou, Chen, Zhang, Zhang, & Qu, 2014). However, there are only a few studies devoted to centrifugal spinning of gum fibers from corn starch (Li, Chen, & Yang, 2016) and blending chitosan with synthetic polymers (Dev, Thinakaran, & Neelakandan, 2015; Li et al., 2019, etc.). To the best of our knowledge, there is no report on the centrifugal spinning of various natural gums with added vitamins for cosmectic applications.

In this work, centrifugal spinning was used for the preparation of gum fibers from aqueous solutions of gum arabic (GA), xanthan gum (XA), and gum karaya (GK) with optimal viscosity and various mass ratios. The solutions contained also poly(ethylene oxide) and both vitamin E and vitamin C. The resulting fibers were analyzed by scanning electron microscopy (SEM) and Fourier-transformed infrared spectroscopy with attenuated total reflectance (FTIR). The most promising fibers were incorporated with vitamins E and C and investigated for the release of vitamin E. The specific role of vitamin C helping in the regeneration of vitamin E from its oxidized form was also assessed.

2. Experimental

2.1. Materials used for centrifugal spinning

Gum Arabic (GA) was obtained from Glentham Life Science. Gum karaya (GK), xanthan gum (XA), poly(ethylene oxide) (PEO), vitamin E ((+)-α-Tocopherol), and vitamin C (ascorbic acid), were purchased from Sigma-Aldrich. Distilled water was used as a solvent for all spinning solutions used in this work. Molecular weight was determined by gel permeation chromatography (GPC) consisting: an isocratic pump, autosampler, multi-angle light scattering detector, and differential refractometer. For data evaluation was used ASTRA software. Molecular weight was achieved ~600,000 g mol^{-1}, ~ 660,000 g mol^{-1}, ~ 2,000,000 g mol^{-1}, and ~ 8,300,000 g mol^{-1} for PEO, GA, XA, and GK, respectively. The hydrodynamic volume is expected to strongly depend on the molecular weights of the polymers used (Farah, Kunduru, Basu, & Domb, 2015). Therefore, therefore it is to be expected that the hydrodynamic volume will be the lowest for Gum Arabic and the largest for Gum Karaya.

Following chemicals were required for the release tests: Iron(III) chloride (FeCl$_3$), Bathophenantroline and Cetrimonium chloride (CTAC), and vitamin E ((+)-α-Tocopherol). All were purchased from Sigma-Aldrich. Ethanol (Penta) and xylene (from Sigma-Aldrich) were used as solvents. Four stock solutions were prepared for the subsequent vitamin release tests: The FeCl$_3$ solution (1) is used as oxidation agent, where Fe^{3+} is reduced to Fe^{2+} by reaction with vitamin E. Fe^{2+} ions then react with Bathophenantroline solution (2) creating colour complex. The spectrophotometric measurement is carried out in an acidic environment made by orthophosphoric acid (3). The solutions of vitamin E (4) are used for the three-point calibration to confirm linearity (the concentrations are 1.6, 3.2 and 4.8 mM).

2.2. Preparation and characterization of the centrifugal spinning solution

Aqueous solutions of these compositions: GA:PEO, XA:PEO, and GK:PEO were prepared in various mass ratios of gums (0.5, 1, 2, 3, and 6) mass and fixed mass ratio of PEO (1). Subsequently, vitamin E and

vitamin C were added to the selected solutions in amounts of 27 wt% and 8 wt% (related to the dry mass, i.e., without water), respectively. A 30 g total solutions were prepared from each mass ratio and stirring at ambient laboratory temperature All blend solutions of gum and PEO were stirred overnight. Vitamin E and vitamin C were added to the gums:PEO solutions and were stirred for 24 h and 2 h prior to the fiber preparation, respectively. Notably, all the used gums were well soluble in water, except the original GK (OGK) that only swelled rather than dissolved in water. Thus, it was necessary to deacetylate it prior to the main spinning solution preparation. Based on a previous study (Poštulková et al., 2017), the deacetylation method was performed for OGK used in this work. Firstly, the solution of OGK 2 wt% was prepared in aqueous media, following stirring on magnetic stirrers at room temperature, and gently stirring overnight. The deacetylation was carried out by adding NaOH (1 mol /l) in a volume ratio of 1:3 to the dispersions of the OGK and adjusting pH with a diluted HCl (0.5 mol /l). The deacetylated GK solution was centrifuged to remove any undissolved particles and the modified GK was precipitated with ethanol. Finally, the product was freeze-dried (lyophilizer Martin Christ Epsilon 2-10D, at −35 °C under 1mBar for 15 h followed by secondary drying process at 25 °C under 0.01 mBar until the change in pressure was up to 10 %).

The rheology of the prepared solutions was assessed by ARES-G2 (TA Instruments, USA) rotational rheometer with a 25 mm parallel plate geometry at 25 °C and the gap of 500 μm. The samples were conditioned for 150 s prior to the measurement to allow relaxation of the stress induced upon the sample loading into the geometry. Frequency sweep oscillatory tests were performed in the range from 0.05 to 50 Hz at the strain amplitude of 1 %. The strain sweep oscillatory tests were performed in the range from 0.1 to 100 % deformation at the frequency of 1 Hz. Notably, the test has covered both the small-amplitude (SAOS) as well as the large-amplitude oscillatory shear (LAOS) as it exceeded the linear viscoelastic region (LVR).

2.3. Centrifugal spinning and characterization of results fibers

Fibers were prepared from the above-stated solutions by the centrifugal spinning pilot tool Cyclon Pilot G2 (Pardam Nano4Fibers Ltd., Czech Republic) described previously (Rihova et al., 2021). Fibers were prepared using following processing conditions: rotational speed 10,000 rpm, temperature 35 ± 5 °C, and relative humidity 25 ± 5 % RH. The resulting fibers were collected in the form of bulky 3D structures in plastic foils.

Morphological analyses of the preparation polymer fibers were carried out by a scanning electron microscope MIRA3-XMU (Tescan, Czech Republic) at the acceleration voltage of 5 kV using a standard Everhart-Thornley secondary electron detector. The samples were coated with a sputtered gold layer (20 nm) using a coater EM ACE600 (Leica, Germany) to avoid charging effects. Spectroscopy using a Vacuum FTIR Vertex70v spectrophotometer (Bruker, Germany) with single-bounce diamond ATR crystal was employed for the compositional analyses of produced fibers in the early stages of all experiments, without added vitamins. Absorbance was measured as a function of the wavenumber ranging from 4000 cm^{-1}-700 cm^{-1} with the resolution of 2 cm^{-1} and the number of scans equal to 64.

The degree of substitution (acetylation) of the starting GK has been examined by NMR spectroscopy with a Bruker AVANCE III spectrometer equipped with a cryoprobe at 500 MHz (number of scans = 80). NMR spectra of saturated solutions in D_2O (a gel) were measured at 60 °C. The chemical shifts are reported in ppm relative to tetramethylsilane. The overall integral peak area was normalized to 100. We have compared the peak areas at 1.87 ppm (CH_3 of the acetyl groups) with that of anomeric protons of the polysaccharide backbone (3.0–4.2 ppm). The methodology has been adopted from Vellora, Padil, Senan, & Černík (2015).

The presence of vitamins in the final samples was evaluated at room temperature by two complementary techniques: i) Raman spectrophotometer MultiRam (Bruker Optik). The YAG:Nd^{3+} laser line (1064 nm)

was used for excitation, ii) FTIR spectrometer Vertex 70v (Bruker, Germany). Conditions of measurement were the same as for the characteristics of Gum:PEO fibers (described above).

2.4. In-vitro release and determination of vitamin E

The in vitro release was performed using GA:PEO fibers (2:1) containing 27 wt% VE and 8 wt% VC (calculated as the entire content of the dry matter). 300 mg of these fibers were immersed into the 40 g paraffin emulsion (prepared by mixing paraffin 48 g, phosphate buffer (pH = 7) 1 g, CTAC 0.19 g, and ethanol 96 % p.a. 1 g). The release of the lipophilic component of prepared fibers was conducted into the paraffin emulsion, stirred by a magnetic stirrer at 250 rpm and 25 °C. At the specific intervals (15, 30, 45, 60, 120, and 240 min), 0.5 g of the emulsion was taken (without fibers) for further analysis of the vitamin release. The removed amount of emulsion was replaced by clear paraffin emulsion of the same weight. In total, 3.5 ml (7 × 0.5 ml) of emulsion was removed from the initial paraffin base emulsion (40 g) and replaced by a clear paraffin.

Each of the 0.5 g of the removed emulsion was mixed with 1.5 ml ethanol/water (1:1) and 6 ml xylene, then vigorously shaken for 2 min. After extraction of vitamin E to xylene (which created an upper layer of nonpolar part of the solution, while the polar aqueous part created a lower layer) the solution was placed into the freezer (−20 °C) for 8 h. This freeze-drying was done for a better separation of upper xylene and lower aqueous layers. In the next step, the 4 ml xylene layer was taken for analysis of vitamin E according to Rutkowski and Grzegorczyk (2007). The 1 ml of $FeCl_3$, Bathophenantroline, and orthophosphoric acid stock solutions described above were added to the xylene layer. After mixing for 2 min, the solution was measured by UV-VIS spectrophotometer (Shimadzu UV-3600 Plus, Japan) at 535 nm wavelength using a quartz glass cuvette (1 cm width). The concentration of vitamin E was subsequently assessed from the calibration curves (concentration of vitamin E vs. absorbance). The cumulative amount released at each sampling time is the sum of the amount in the receiver at that time plus the amount in each sample that was removed and replaced with empty buffer. The last point is taken as 100 %. Concentration at each point is devided by concentration at the last point x 100. The cumulative release of vitamin E was measured according to the following formula:

$$M_n = C_n V + V_1 \sum_{i=1}^{n} C_{n-1} \tag{1}$$

$$W = \frac{M_n}{M} \times 100\% \tag{2}$$

where Mn and Cn are cumulative mass and concentration of the vitamin E at specific times and W is a cumulative release of vitamin E at a specific time.

The calibration set of pure vitamin E was measured similarly as the sample of GA:PEO fibers + VE and VC (by UV-VIS spectrophotometry), except that this sample's emulsion (0.5 g) was replaced by 0.5 g of stock solution of vitamin E (of different concentrations), mixed with 1.5 ml of 50 % ethanol and 6 ml of xylene, followed by 2 min of extraction. In the next step, 4 ml xylene layer was taken for analysis, mixed with 1 ml of all remaining stock solutions for 2 min, and submitted to UV-VIS spectrophotometry to obtain data for the calibration curve.

To verify, if vitamin C is also released or not, the GA:PEO (2:1) fibers with only vitamin C were prepared in the same way as with vitamin E. The sample was treated the same way and underwent the same spectroscopic determination as for vitamin E. The results showed that vitamin C does not influence the determination of vitamin E.

3. Results and discussion

3.1. Optimization of spinning solutions for the synthesis of fibers from gums and poly(ethylene oxide)

At first, solutions composed of gums only were not spinnable, as it turned our during preliminary experiments. Since the literature reports on the positive effect of PEO contribution on the spinnability (by electrospinning) of otherwise non-spinnable polymers (Padil & Černík, 2013), it was decided to prepare mixed solutions of gums with different ratios of PEO. The goal behind was to find the most suitable compositional ratio between the used gums and PEO for high quality fibers by centrifugal spinning. The effect of gum addition (GA, XA, and GK) was investigated for selected fibers with a gum mass ratio from 0.5 to 6 against PEO. The resulting spinnability of solutions of different mass ratios of used gum is summarized in Table 1.

Interestingly, the spinnability of the gums scaled with their molecular weight and decreased in the following order: GK > XA > GA, as shown in Table 1. The relatively low molecular GA was able to produce fibers at almost all tested GA:PEO ratios, while the higher molecular XA and GK yielded fibers only at two and one gum:PEO mass ratios, respectively. In other ratios, only spraying occurred upon the spinning, yielding massive production of droplets instead of fibers. More specifically, GA:PEO fibers could be prepared up to the mass ratio of 3:1 (GA:PEO), while further increase to 6:1 (GA:PEO) caused spraying. Most likely, this is caused by overcoming a critical concentration of GA, which leads to entangled macromolecules and thus insufficient gums-PEO interactions needed for fiber formation.

XA:PEO and GK:PEO fibers (without visible spraying) could be prepared up to the mass ratio of 1:1 and 0.5:1, respectively, while spraying was observed at higher gum:PEO mass ratios. According to Mukherjee et al. (2010), gums have ionic carboxyl groups, which participate in dipolar, ion-dipolar, and hydrogen bonding interactions with other materials in the solution. GA, XA, and GK consist of various mixtures of monosaccharides, especially with carboxyl groups (galacturonic and glucuronic acids) located in the gums' concentration range from 3 to 28 % (Anderson, Bridgeman, Farquhar, & McNab, 1983; Dave & Gor, 2018). In this case, the reduced fiber production could be caused by weak hydrogen-bonding interactions between the functional groups of the used gums and PEO.

As already mentioned, viscosity is one of the determining processing factors for fiber preparation by centrifugal spinning. Therefore, the viscosity of the pure PEO solution and blend mixtures (gums and PEO) with various gum mass ratios were assessed by a rotational rheometer under oscillatory shear. Fig. 1A–C shows the complex viscosity as a function of the oscillation frequency for the PEO mixtures with GA, XA, and GK, respectively, and Fig. 1D depicts the zero-shear viscosity at 1 Hz and the power-law index n as a function of the gum concentration. The former characterizes the undisturbed structure at rest while the latter is indicative of the viscosity depression in the shear-thinning region following the equation:

$$\eta(\gamma') = k\gamma'n - 1$$

Table 1

Spinnability of solutions of different mass ratios of gum and poly(ethylene oxide) (Gum/PEO): *f* indicates the formation of fibers, *s* indicates the formation of fibers with the visible spraying of droplets, *x* indicates spraying (i.e., no formation of fibers). Note that GA, XA and GK were not spinnable themselves (i.e. without PEO addition).

Spinnability	Mass ratio				
	0.5:1	1:1	2:1	3:1	6:1
GA:PEO	*f*	*f*	*f*	*f*	*s*
XA:PEO	*f*	*f*	*s*	*x*	*x*
GK:PEO	*f*	*s*	*x*	*x*	*x*

where the variables η, γ', and k represent viscosity, shear rate, and consistency. The oscillation frequency, angular frequency, and shear rate could be interchanged (1 Hz $\approx$ 1 rad·s^{-1} $\approx$ 6.28 s^{-1}) according to the semi-empirical Cox-Merz rule for rheologically simple liquids which allows to directly compare the simple-flow viscosity η with the complex viscosity η* determined from oscillatory tests. The viscosity in the power-law region is given by the balance between the rate of the chain orientation in the shear field, often connected with disruption of weak intermolecular forces, and the rejuvenation to the zero-shear condition (Hyun et al., 2011). Hence, the power-law index is indicative of the intermolecular forces within the polymer liquid.

The viscosity of the GA:PEO solutions increased only indistinctly with the growing PEO concentration within the GA:PEO mass ratio range of 0.5–2:1 (Fig. 1D). Slightly elevated viscosity was recorded for the GA:PEO mass ratio of 3:1 over the whole frequency range while the GA:PEO of 6:1 increased the viscosity only at frequencies above ca 5 Hz (Fig. 1A). In turn, the zero-shear viscosity of the GA:PEO 6:1 is comparable to the GA:PEO 0.5–2:1 while the power-law index steadily rose with the increasing gum concentration. The drop in viscosity at high GA content likewise corresponded with the limited miscibility of the GA: PEO solution and was accompanied by visible inhomogeneities in the solution. On the other hand, the elevated n indicated weaker intermolecular bonding within the solution at high gum content.

A much higher viscosities were achieved for XA:PEO than for GA: PEO solutions (Fig. 1B) as would be expected for a polysaccharide with higher molecular weight. The zero-shear viscosity of XA:PEO showed a systematic increase with the increasing gum concentration (Fig. 1D). The well spinnable XA and GA formulations (XA:PEO up to 1:1, GA:PEO up to 3:1) hugely mismatched in their zero shear-viscosities (Fig. 1D), which means that it could not be used as a simple parameter correlating with the expected fiber formation (Table 1).

The low values of the XA solutions' power-law index mark the strongest intermolecular interactions within the tested gums. On the other hand, the power-law index of the GK:PEO 0.5:1 revealed very weak intermolecular forces in this solution (Fig. 1D). This finding likely explains its lower zero-shear viscosity compared to the XA:PEO solution of the same mass ratio, despite GK had a higher molecular mass than XA. The viscosity reflects the amount of inner friction which depends not only on the molecular mass but is also enhanced by stronger interactions within the sample. An increase in the GK content to GK:PEO 1:1 substantially increased the zero-shear viscosity as well as strengthened the intermolecular forces (Fig. 1D). Despite these values were closely matching those of the well-spinnable XA:PEO 0.5:1 (Table 1), the compromised spinnability of GK:PEO 1:1 (Table 1) serve as clear evidence that the spinnability is not a simple function of the zero-shear viscosity and power-law index of the gum:PEO solutions.

3.2. Fiber morphology

Fig. 2 presents scanning electron microscopy (SEM) images of fibers prepared in various gum:PEO mass ratios. At the first glance, the morphology and structure of all the prepared fibers looked similar. However, a detailed evaluation revealed debonding (as indicated in the corresponding image by arrows) of GA and PEO fibers prepared with a mass ratio of 3:1. This fact can be caused by the weak hydrogen bonds between GA and PEO resulting in insufficient fiber cohesion and correlates well with the rheological findings (Fig. 1D). Apparently, the damage was largely also observed at increased GA content of GA:PEO 6:1. Nevertheless, a substantial formation of fibers with spraying (Table 1) was achieved at this GA concentration, which could mean that the weakly-bonded GA achieved insufficient spun fibers.

These are results comparable to previous reports on the preparation of complex (gums + synthetic polymers) fibers from aqueous solutions (Dror et al., 2003; Lu, Zhu, Guo, Hu, & Yu, 2006; Islam & Karima, 2010; Padil & Černík, 2013; Ranjbar-Mohammadi et al., 2013; Lubamboa
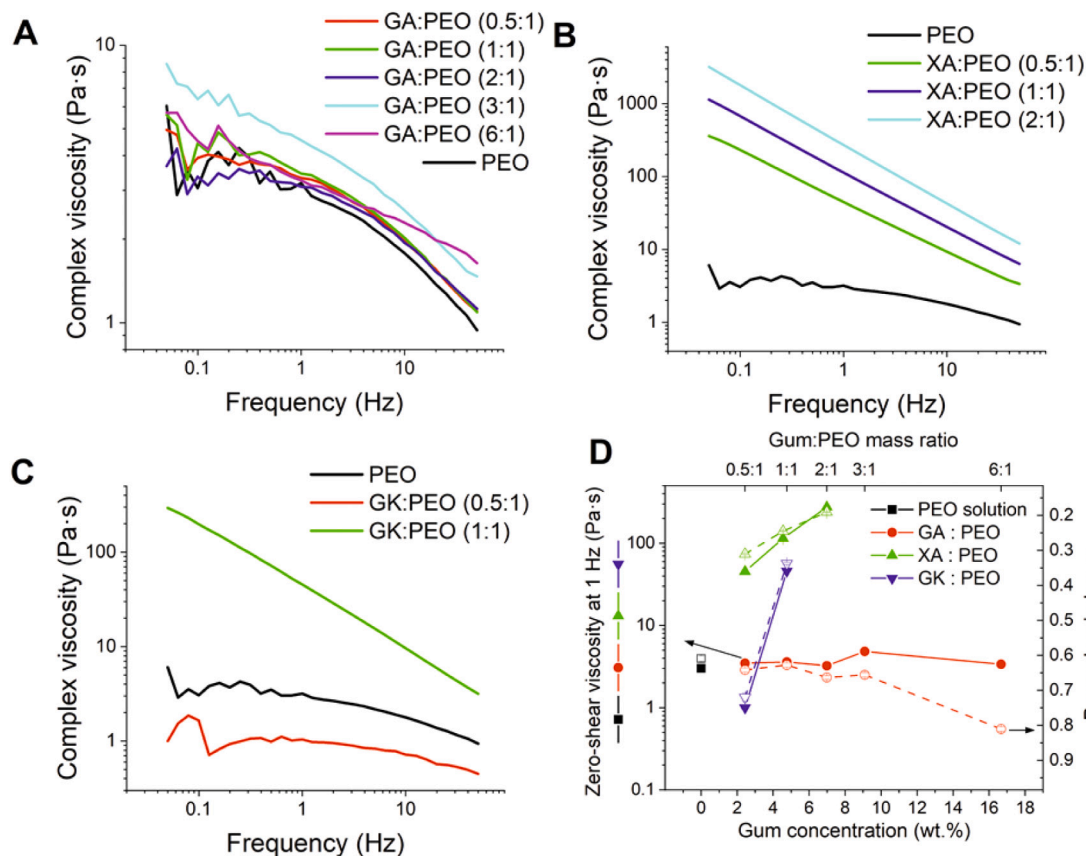
Fig. 1. Complex viscosities as a function of frequency at 1 % strain amplitude for different blend solutions: (A) GA/PEO, (B) XA/PEO, (C) GK/PEO. (D) Zero-shear viscosity and power-law index dependence on the gum concentration at 1 Hz. The direction of the right y-axis representing the power-law index is inverted to highlight the differences between the two functions.

et al., 2013; Patra, Martincová, Stuchlik, & Černík, 2015; Rezaei, Tavanai, & Nasirpour, 2016; Padil et al., 2016, etc.). For example, Dror et al. (2003) showed the fiber preparation from a blend of GA, PEO, and multiwalled carbon nanotubes at the GA concentrations of 1 % (w/w), 4 % (w/w), and 0.35 % (w/w), respectively. Padil et al. (2016) reported a fiber preparation from GK (3 wt%) and GA (10 wt%) blend solutions with PEO and PVA with the concentration of 10 wt% under various mass ratios of the gums and synthetic polymers. Their results showed that using PVA in blend with GK and GA led to better spinnability than the PEO. The fiber preparation is also dependent on the chemical properties of the used polymers. With the increasing molecular weight of the polymer, the viscosity increases, and fibers are better formed (Colmenares-Roldán, Quintero-Martínez, Agudelo-Gómez, Vinasco, & Hoyos-Palacio, 2017; Koski, Yim, & Shivkumar, 2004; Mwiiri & Daniels, 2020). On the other hand, too high viscosity may prevent jet formation due to resulting forces being insufficiently low. Since Padil et al. (2016) did not provide the molecular weight of the synthetic polymers used in the study (PVA and PEO), it is not possible to compare their study with the current one. Thus, a direct and more detailed comparison of the literature with the current work is difficult. It should be noted that this work is the first report on the successful preparation of centrifugal spun fibers based on water-soluble and readily available natural gums (GA, XA, and GK).

The presence of used gums in the prepared blend fibers was confirmed by using FTIR analysis. FTIR spectra of the blend (gum:PEO) fibers are shown in Fig. S1 (A, B, C) for GA:PEO, XA:PEO and GK:PEO, respectively. All thee spectra in Fig. S1 show spectra of corresponding pure gums. Fig. S1C also shows spectrum of pure PEO reference for reference. From all these results it is clear, that the all blend fibers are composed corresponding gums and PEO, according to expectations. In

addition, all spectra of the blend fibers showed the presence of absorption peaks at approx. 1600 cm^{-1} corresponding to the asymmetrical stretching (νas) vibrations of COO- carboxylate groups. The bands near 1410 cm^{-1} are associated with COO- symmetrical stretching modes (Appolonia Ibekwe, Modupe Oyatogun, Yodeji, & Michael Oluwasegun, 2017; Mohsin et al., 2018; Poštulková et al., 2017). Moreover, there is a peak at 1730 cm^{-1} that appears for XA blend fibers and at 1723 cm^{-1} for OGK fibers, that should be assigned to the acetyl groups of xanthan (karaya) polysaccharide ester bond vibrations. The next band associated with vibrations in acetyl esters is located at ~1240 (1236) cm^{-1} (Mohsin et al., 2018). In case of GK fibers, the band at 1723 cm^{-1} disappears and intensity of band at 1236 cm^{-1} is significantly reduced which confirms deacetylation of OGK. The next common wide bands with a maximum between 3600 and 3000 cm^{-1} for the prepared fibers were associated with the peak of -OH stretching, attributed to the gum in the fibers (Appolonia Ibekwe et al., 2017; Mohsin et al., 2018; Poštulková et al., 2017).

The molecular structure, especially degree of acetylation, of the used gums was investigated by NMR spectroscopy. Based on the integral intensities shown in Fig. S2, we can roughly estimate the content of the acetyl groups to 10.5 %, which is within the scope of the reported values for karaya polysaccharides (8–12 %) (Brito, Silva, de Paula Silva, & Feitosa, 2004). NMR spectroscopy has also been employed to determine the degree of deacetylation. When assigning the diminished signal at 1.77 ppm (Fig. S3) to residual acetyl groups of GK, the residual content of the acetyl groups has been calculated below 0.5 %. Hence, we can consider the deacetylation as almost complete. Due to the high molecular weight, it is difficult to determine the composition of sugars. There are some studies (Setia, Goyal, & Goyal, 2010; Lujan-Medina et al., 2013; Patra, 2019 etc.) that showed sugar composition in the GK. Only
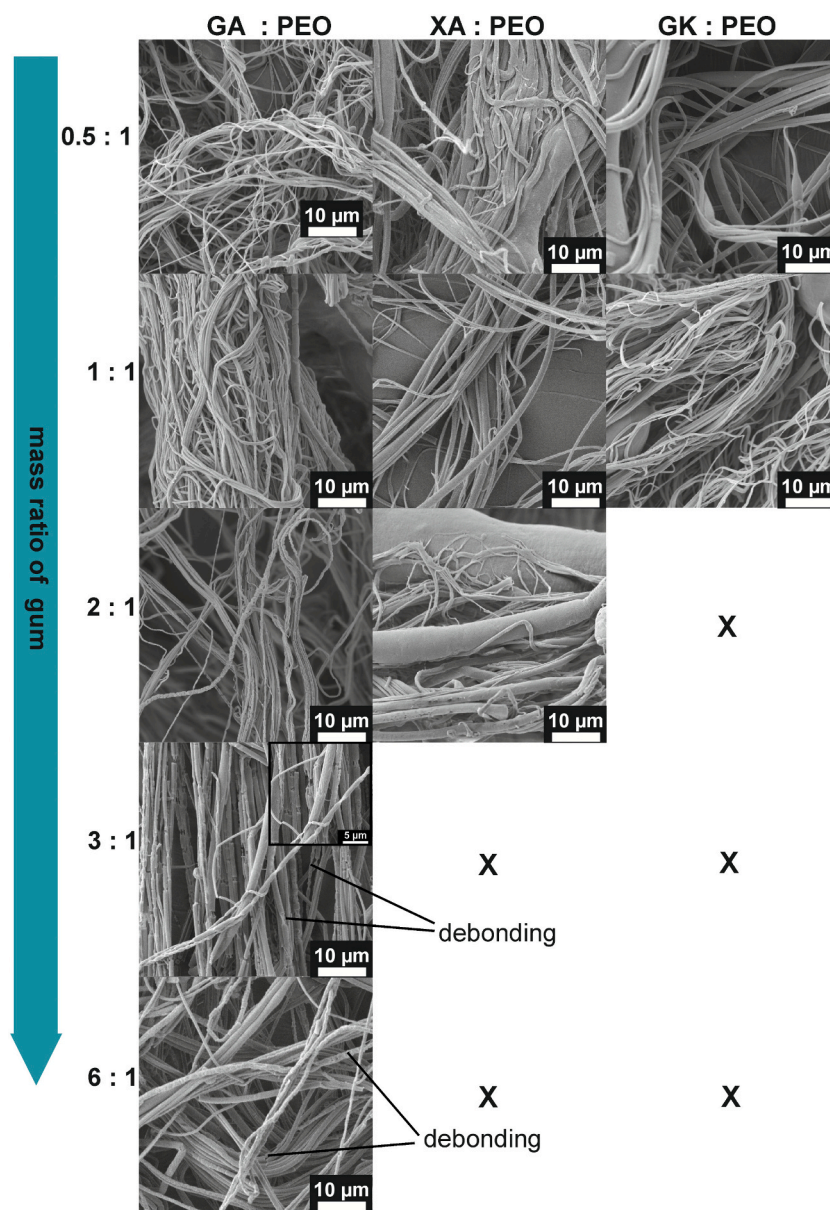
Fig. 2. SEM images for blend fibers from gums and PEO obtained under various mass ratios of gums, "x" indicates no prepared fibers.

Brito et al. (2004) determined by high performance liquid chromatography the sugar composition in GK after deacetylation. However, a more detailed analysis of the effect of deacetylation cannot be done because the same type of GK was not used in above mentioned studies. Because the presence of acetyl groups is predominantly oriented on the uronic acid residues, it is probable that the direct sugar composition was not rapidly affected during deacetylation.

Since obtained results in this work showed very interesting trends for the preparation of fibrous materials based on natural gums, the selection of fibers for further analysis was based on these criteria– the biggest amount of used gum fibers produced per given process (i.e. theoretical highest yield) and the successful formation of fibers without visible morphological defect (i.e. spinnability). Using these criteria, we chose these fibers: XA:PEO (1:1), GK:PEO (0.5:1) and GA:PEO (2:1) based on their fiber formation (Table 1, Fig. 2). The FTIR spectra of the selected samples, i.e. GA:PEO 2:1, XA:PEO 1:1, and GK:PEO 0.5:1, are captured in Fig. 3. It can be seen that the functional groups of the gums used were present in the prepared blended fibers. The assignment of these groups is already mentioned in the text above.

3.3. Influence of addition of vitamins E and C on the morphology of resulting fibers

Since the addition of gum used to prepare fibers was observed to play an important role in fiber formation, vitamin E (VE) and vitamin C (VC) were added to the selected solutions: GA:PEO (2:1), XA:PEO (1:1), and GK:PEO (0.5:1) based on the optimization, as described above. While the blend fibers containing GA, PEO, VE, and VC were successfully prepared, the polymer fibers containing XA or GK with the addition of vitamins were not formed. This fact can be explained by the emulsifying ability of GA causing homogenous dispersion of vitamin E oil phase in aqueous medium (PEO solution). Some previous studies (McNamee, O'Riordan, & O'Sullivan, 1998; de Paula, Martins, de Costa, de Oliveira, & Ramos, 2019; Zhang et al., 2019, etc) demonstrated the positive effect gum arabic on the emulsifying properties of solutions.

An addition, the too high viscosity of the blend solution XA (Fig. 1B), which could cause the insufficient mixing of the XA and PEO aqueous phase with the oily phase which consisted of natural vitamin E. On other hand, for GK and PEO solutions were not observed so high viscosities
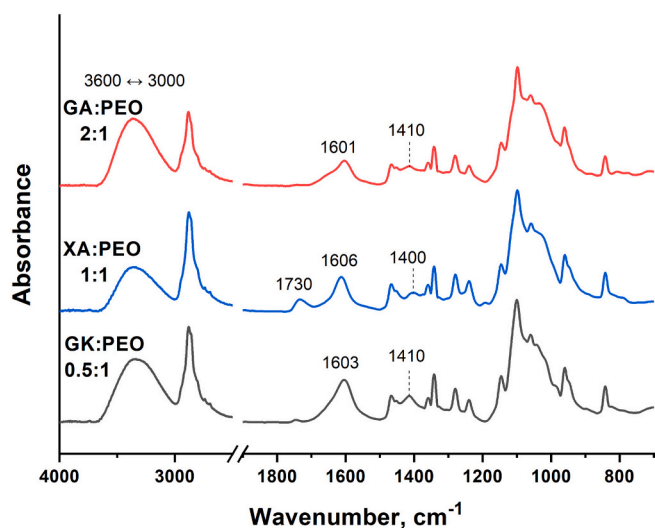
Fig. 3. FTIR spectra for the selected fibers prepared from: gums (GA, XA, and GK) and PEO. The marked peak corresponds to the carbonyl group (C=O) of the polysaccharide gums.

(Fig. 1C), the smallest addition of GK could cause already insufficient hydrogen bond interactions between the carboxyl group of GK and the hydroxyl group attached to the aromatic ring of vitamin E and thus to the non-spinnability of the blend solutions used.

SEM images of the GA and PEO fibers and fibers with the addition of vitamins (VE and VC) are shown in Fig. 4A-and B. This comparison shows that GA:PEO fibers incorporated with both vitamins (VE and VC) kept fibrous structure without visible defects. However, by a detailed inspection of this figure, one can see that the fibers after addition vitamins E and C visible changed their diameter. Namely, compared with GA:PEO fibers, the addition of both vitamins rapidly increased fibers diameters from 596 nm ($\pm$186) to 904 nm ($\pm$284). This increase in fiber diameters can be attributed to the addition of an oil phase (in this case VE) to the aqueous phase. As a result, these fibers possess significantly increased diameters. For comparison, pure PEO fibers (without and with the addition of both vitamins) were also prepared from differently concentrated PEO solutions. However, regardless of the PEO concentration, the used rotation rate, and the presence of vitamins, these solutions did not yield high-quality fibers, but rather droplets, as can be seen from illustrative SEM images in Fig. S4. In the light of our previous publication (Rihova et al., 2021), one can clearly conclude that pure PEO solutions possess very poor spinnability into fibers. Nevertheless, the addition of both vitamins did not significantly affect the PEO fibers´

diameters (among the droplets). There was only a moderate increase from 447 ($\pm$165) nm to 596 ($\pm$222) nm, respectively. These PEO result clearly justify the need of using the mixed gum:PEO solutions for the preparation of high quality fibers.

The presence of vitamins in the blend of fibers (GA:PEO + VE, VC) was confirmed by FTIR spectroscopy. As is shown in this Fig. 5, for detailed analysis and interpretation of obtained results were analyzed individual participant spectra of vitamins and VE loaded in fibers. The prepared fibers display characteristic absorption bands marked peak corresponds showing the presence of VC. As shown in this figure, there are two peaks assigned to the VC in the prepared fibers. The absorption peak observed at 1748 cm^{-1} is clearly assigned to the C=O stretching, whereas the peak at 1675 cm^{-1} is attributed to the vibration of the C—C group localized in the aromatic ring in VC.

While the functional (carboxyl) group of VC is very visible in FTIR, the vibrations of functional groups of VE are overlapped with vibrations of functional groups of PEO in the whole IR spectral region. Thus, to verify the presence of VE in fibers, Raman spectroscopy had to be used. The Raman spectra of individual VE, VC, and GA:PEO fibers incorporated with both vitamins (VE and VC) are depicted in Fig. 6. In the case of VE and VC-loaded fibers (red curve), we can clearly distinguish in the region between 1400 and 1640 cm^{-1} bands at 1438, 1480, 1585 a 1618 cm^{-1}. The band at 1480 cm^{-1} has its origin in bending vibrations of
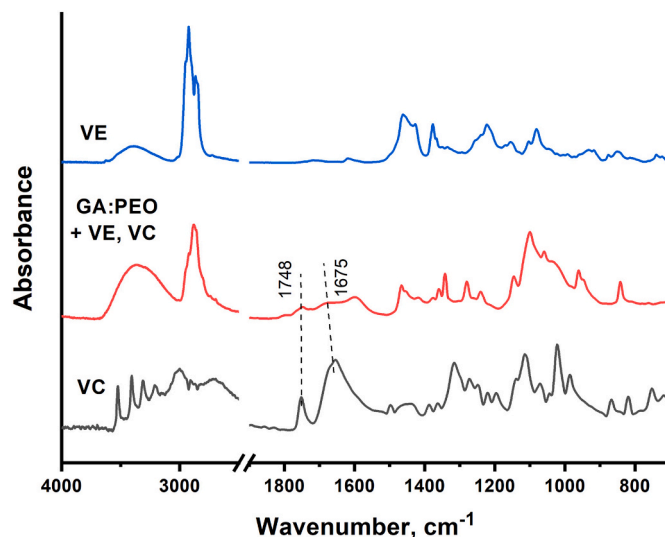

Fig. 5. FTIR spectra for individual vitamins - VE, VC, and for fibers GA:PEO + VE, VC. The marked peaks correspond to the functional groups of the VC.
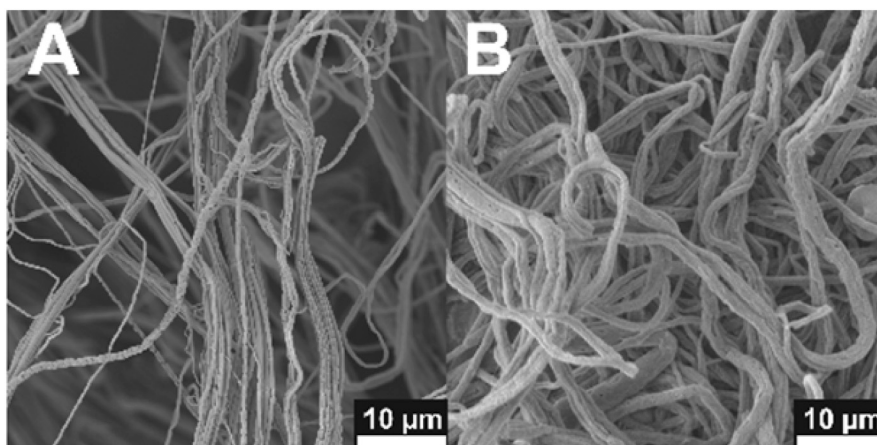

Fig. 4. SEM images of centrifugal spun fibers: (A) GA:PEO and (B) GA:PEO + VE, VC.
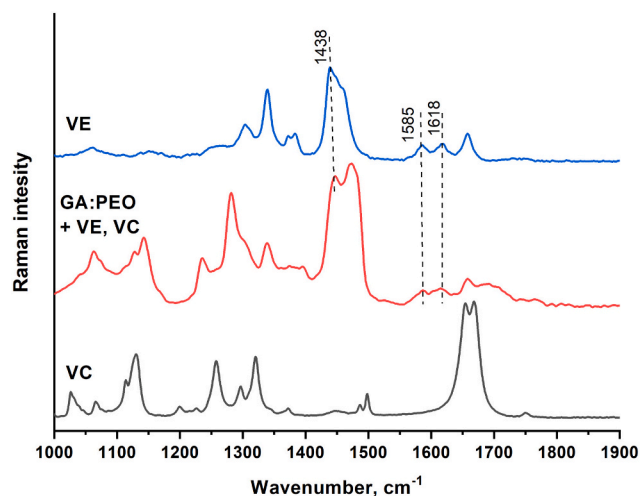
Fig. 6. Raman spectra for vitamins - VE, VC, and for fibers GA:PEO + VE, VC. The marked peaks correspond to the functional groups of the VE.

C—H bonds in PEO (Sim, Gan, Chan, & Yahya, 2010). Other peaks are associated with vibrations of VE. The peak at 1438 cm^{-1} is attributed to the bending vibrations of the C—H bond, peaks at 1585 and 1618 cm^{-1} can be assigned to the stretching vibration of the aromatic ring localized in α-Tocopherol (chemical form of VE) (Beattie et al., 2007). These results are confirmation of the presence of VE in the prepared GA fibers.

3.4. In vitro release vitamin E

Fig. 7 shows the percentage of VE released from GA:PEO fibers with incorporated both vitamins (E and C). It can be seen, the release of VE-loaded centrifugal spun fibers showed a burst release during the first 15 min with ~72 % release of VE and after immersion for 45 min, the cumulative release was reached almost 100 %. Thus, the fast-release of VE obtained in this work can indicate the presence of VE on the surface of the prepared fibers. For comparison, the release of VE from PEO fibers (spun without GA) was also investigated, as shown in Fig. S5. It exhibited first burst release during 15 min only ~25 % and at 180 min, the cumulative release VE was reached 100 %. This burst is very likely connected to the fact that only a limited mass of the spun PEO materials was converted into fibers (as shown in Fig. S4). Thus, this reference material was not further investigated in this work.

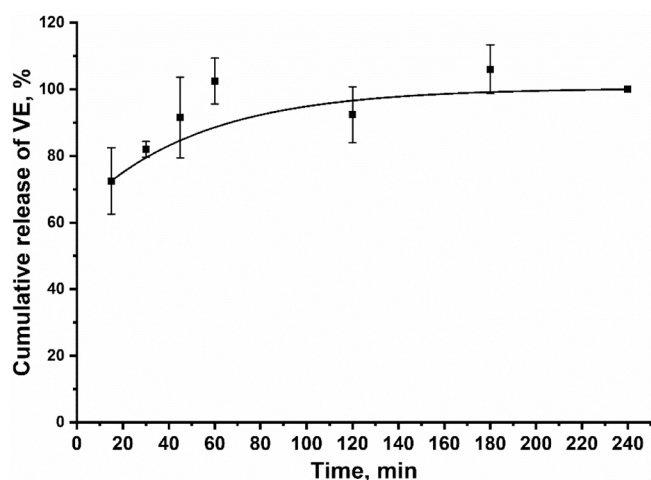It is known, that VC protects VE from its oxidation and thus was

Fig. 7. Release of vitamin E from GA:PEO fibers with incorporated vitamins E and C.

added to the solution (GA, PEO, and VE) used for the preparation of fibers. Since VC belongs to the group of antioxidants, it was necessary to confirm that only VE is released during the process of this process. These experiments were conducted in exactly the same manner as for VE, but without any VE content (see Experimental part for details). Table S1 shows that no significant release of VC took place during the identical release times used for the VE release. This is due to the fact that VC belongs to group vitamins soluble in polar solvents and cannot dissolve in non-polar solvents. In contrary, VE is soluble in non-polar organic solvents, which were used in this work for extraction (see Experimental part for detail). Therefore, it is clear that the extraction of vitamins used in this study could only yield release of VE and not VA. Thus, it can be stated, that only VE is released from the fibers in the given solutions used in this work.

The herein presented results with very VE release contrast with the early reports (Taepaiboon et al., 2007; Dumitriu, Stoleru, Mitchell, Vasile, & Brebu, 2021; Li, Wang, et al., 2016). Namely, Taepaiboon et al. (2007) reported the effect of VE-loaded electrospun fibers from cellulose acetate. They showed that amount of released VE gradually increased and after 24 h it reached ~52 %. Dumitriu et al. (2021) reported the release of poly(ε-caprolactone) fibers with incorporated VE with different concentrations (1, 5, and 20 %). Their study showed that during the burst release (12h) the fibers with a higher amount of incorporated VE (5 % and 20 %) released ~16 % of VE, while the fibers with the lowest amount (1 %) released only ~8 % of it, respectively.

Two reports utilized synthetic VE. Li, Wang, et al. (2016), whose prepared electrospun fibers from gelatin with incorporated VE achieved a very slow release. Their results showed that the gelatin fibers with VE showed ~30 % release during the first 10 h and after 68 h the maximum VE release reached ~72 %. Furthermore, vitamin A was also added to the VE-loaded gelatin fibers to protect the VE from oxidation. The resulting fibers showed that the addition of vitamin A did not affect the release of the VE, because fibers incorporated with both vitamins reached a similar amount of VE release, such as for the gelatin fibers with VE incorporated only.

However, in contrast to the literature (Taepaiboon et al., 2007; Dumitriu et al., 2021; Li, Wang, et al., 2016), the centrifugal spun fibers prepared from GA, PEO, VE, and VC in the present work possess larger fibers diameters in comparison with electrospun fibers (typically are up to 500 nm). This finding is very important, because it showed that fibers diameters have very likely an influence on the speed of the VE release.

In general, a slow-release is required mainly for the clinical applications, due to the need for an extended-release of the active substance for the topical treatment of severely damaged skin that requires rather long time (Taepaiboon et al., 2007; Dumitriu et al., 2021; Li, Wang, et al., 2016).

However, there are some applications, where the fast release of active components is required. For example, for the treatment of skin (within the daily skincare and skin regeneration) various creams and hydrogels that contain active components are usually used with a fast release of the maximum dose of active ingredients in a short time (scale of minutes to a few hours). Thus, VE-loaded GA:PEO fibers prepared in this work could have the potential for these applications.

In general, commercial products like creams, films and hydrogels have shortcoming. Especially in easy contamination and prevention of skin ventilation. Thus, the developed fiber masks could overcome some of these *limitation* (Dao et al., 2018; Kaul et al., 2018). *Moreover, these fibers possess distinct advantages* in: i) application- they adhere perfectly to the face, followed a rapid release of vitamin E (i.e. it is not necessary to have this mask on the face for a long time); ii) ecological - they are composed of only 4 components, fiber masks are in dry state not wet - no preservatives are needed, which are usually dangerous allergens; iii) economic - low weight of fibers used and lower number of components will contribute to lower costs of the final product. The real application of these fiber is very simple and can be realized as follows. Firstly, the facial skin is moisturized with water or cream. Subsequently, the fibers are

placed onto the skin and left to react for about 15 min. After this period, the fibers are removed from the skin and that is it. All in all, the herein presented fibers are the first fibers bearing promise for cosmetic and dermatologic applications, as they show many advantages for these applications compared to the discussed literature, but mainly the fast release of an active compound.

4. Conclusion

In this work, centrifugal spinning was used for the preparation of blend fibers composed of natural gums (gum arabic, xanthan gum, and gum karaya) and poly(ethylene oxide). Firstly, the optimization of fiber synthesis was carried out for solutions of various ratios of used gums and a fixed ratio of poly(ethylene oxide). The obtained results showed that a lower ratio of xanthan gum (1) and gum karaya (0.5) was sufficient for fibers preparation, while for fibers based on gum arabic larger ratio of the gum had to be used (2). It was shown that the optimal ratio of gum: PEO in the spinning solutions is an important factor for the spinnability of the fiber. In addition, the optimal ratios in the solutions enabled the synthesis of homogenous fibers, as evaluated by electron microscopy.

The knowledge gained from these experiments was further used for the synthesis of fibers with vitamin content. The different chemical composition and especially the molecular weight of the used gums turned out to be an important criterion for the formation of fibers with incorporated vitamins E and C. At the end, from all three gums investigated here, only GA:PEO fibers loaded with vitamin E and vitamin C could be prepared as homogenous fiber networks as revealed by SEM investigations. Thus, only these fibers were used for further analyses, including vitamin release. Successful incorporation of both vitamins within the fibers was confirmed using FTIR and Raman spectroscopy. In addition, in vitro evaluations of GA:PEO fibers with loaded vitamins showed a burst release of VE during 15 min, while there was no detectable release of vitamin C. Interestingly, the rapid release could be affected mainly due to the large fiber diameter observed for GA:PEO fibers. These findings have shown that the use of GA:PEO fibers with incorporated vitamins E and C have in potential mainly the cosmetic and dermatologic fields, where these rather quick release requirements are often in demand.

CRediT authorship contribution statement

M.R., L.V. and J.M.M. conceived the idea of the paper, M.R. designed the experiments, performed the preparation and characterization of fibers, and wrote the article. P.L. performed analyses of viscosities of spinning solutions and subsequent evaluation, V.C. and L.H. carried out the vitamin release tests, B.F. carried out Raman and FTIR analyses and evaluations, F.B. carried out NMR analyses and evaluations, L.V. and J. M.M. supervised the research. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.carbpol.2022.119792.

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