Fabrication and Characterization of Hazelnut Shell Powders-loaded Poly (lactic acid) (PLA) Composite Fibers

Ilyas Kartal* and Ibrahim Sengor
Department of Metallurgical and Materials Engineering, Faculty of Technology, Marmara University, Turkey.
ilyaskartal@marmara.edu.tr*

(Receivced on 17th August 2020, accepted in revised form 24th October 2022)

Summary: In this research, fibers were obtained by adding hazelnut shell powders which are a natural filler material (HSP) at different concentrations into Poly (lactic acid) (PLA) by using the electrospinning method, which is the most common method to obtain fibers. Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), tensile strength measurement, and physical analysis such as density, surface tension, viscosity, electrical conductivity test was performed after the fiber production process. The results obtained from this study, fibers showed beadles and smooth surfaces. The diameter distribution of these fibers was observed at 2092 µm without hazelnut shell powder. HSP was added to the composites (ϕ=2379,64±635,268 µm for b; ϕ=25581000,339±,806 µm for c; ϕ=2619,24±967,364µm) and diameters were increased. This result had shown, that by increasing the HSP proportion in the PLA/HSP solution, the average diameters of the fibers were increased. The tensile strength of the fibers decreased between the s1-s4 specimens. It has been shown that the tensile strength decreases as the diameter increases. The resulting structures of the fibers possessed antiseptic properties, which are attractive for many biomedical applications.

Keywords: Electrospinning, Poly (lactic acid), Hazelnut shell powder, Fiber.

Introduction

Electrospinning is a versatile and cost-effective method for producing continuous fibers ranging in diameter from 10 nm to several micrometers. Also, electrospinning is a powerful technique for the production of polymeric fibers at micron, submicron, and nanoscale. Due to the random accumulation of fibers, it has a high specific area, very small pore size, and high porosity. Electrospun matrices let obtaining electrospun matrices mimicry the natural construction of extracellular matrix nanofiber structures with flexibility. They have major potential in varied fields such as packaging, optical electronics, biotechnology, defense and security, cosmetics, food, tissue, and environmental engineering [1,2].

Hazelnut shell was obtained from the hazelnut known as hazelnut. Looking at the structure of the hazelnut shell in macro terms, it can be seen that the shell consists of two main layers. The outer one has a hard structure and the inside of this layer is surrounded by a soft, loose layer. Therefore, the ground hazelnut shell contains these two parts. In this study, it was obtained from the hard part of the shell. Since it was planned to use the powder obtained, the soft part was used by separating it. Hazelnut shell powder is cellulosic, relatively hard, abundant, and has a characteristic color. For this reason, the realization of wood appearance by the extrusion process with a mixture of small amounts of process additives brings to mind the use of hazelnut shells as a filler in plastic matrix composites.

Poly (lactic acid) (PLA), produced annually from renewable sources, is a processable synthetic polymer with various ecological advantages. PLA closes the gap between natural and synthetic fibers in many areas ranging from environmentally friendly garments, household appliances, and packaging to medical and pharmaceutical applications. Ease of composting, unique property spectrum, renewable source origin, and ease of melt processing and recycling at the end of its useful living has led to poly (lactic acid) fibres finding rise interest [3].

Production of thermoplastic-based composites using lignocellulosic fibers is enhancing day by day. In this way, thermoplastic composite production has started to become a fast-growing sector in the wood composite industry. Various thermoplastic polymers such as polyethylene (PE), polypropylene (PP), polylactic acid (PLA), and lignocellulosic-based wastes (agricultural wastes, wood flour, etc.) can be used in the production of these composites [4].

*To whom all correspondence should be addressed.

Hazelnut shell, a by-product of the food industry, is an industrial waste. Therefore it is cost-effective and improved. Its exploitation is an amazing problem. This filler might be grounded for giving a lignocellulosic flour that can ensure the polymer composites with a wood-like appearance. The usage of the reinforcement/filler with a broad diversity of polymeric matrices, which are providing the materials with a wood-like appearance and thus contribute to forestry resources preservation [5].

In this study, hazelnut shell powders in different proportions and a biocompatible polymer poly (lactic acid) (PLA) were used. With the combination of these materials, random fibers were produced using the electrospinning technique. Tensile strength measurement, scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and physical analysis (electrical conductivity, density, viscosity, surface tension) measurement was performed after the production process. In this presented study, in Turkey, in the black sea, there are produced and consumed of hazelnut shells that may be provided using as the reinforcing additive in fiber material for biomedical applications by recycling.

Experimental

Materials

Poly (L-lactic acid) (PLA) (120.000 gr/mol) was purchased from Nature Works LLC, Minnetonka, MN. Other chemicals and reagents, e.g., chloroform, Tween80 were employed in the experiments purchased from Sigma-Aldrich. Hazelnut shell powders were used as filler materials. The fillers were collected from Ordu, Turkey. Since the hazelnut shell powder contains the outer and inner parts of the shell together, the necessity of separating the components from each other has emerged. These components were again separated from each other by the traditional airflow method. Various types of sieves were used for the sieving process. In the sieving process, powder composites with a size distribution of approximately 200 microns were obtained.

Producing of hazelnut shell powder

Naturally obtained hazelnut shell was washed with distilled water. Then hazelnut shell was left to dry at room temperature. When the drying process finished, the mixture was pulverized to a few micrometers.

Preparation of the solutions

In our experiments, we prepared four different solutions containing pure PLA and hazelnut shell powders at different rates (Table 1). Initially, we expected to dissolve 10 % of the granular Poly (lactic acid) (PLA) material in 20 ml of chloroform solution for two hours. After dissolution was finished, 3wt% Tween 80 was added into the solution again and stirred for 15 minutes. Then, hazelnut shell powder was put in amounts corresponding to pure, 1%, 2%, and 3% in different ratios respectively, and an ultrasonic mixer was used to provide a homogeneous dispersion of the particles, and mixing was performed for 15 minutes. Care was taken to avoid bubbles forming in the solution.

Determinations of the physical properties of electrospinning solutions

Physical characterizations of four various solutions were performed by using a viscometer, surface tension device, electrical conductivity device, and pycnometer. The density was quantified by using a standard 10 ml density bottle, DIN ISO 3507- (Boru Cam, Turkey). The electrical conductivity of the solutions was measured using a conductivity probe (Cond 3110 SET 1, Germany). The surface tension values of the solutions were measured with a force tensiometer (Sigma 703D, Attention, Germany) with a platinum ring. The viscosity values of the suspension were measured by a digital viscometer (DV-E, Brookfield AMETEK, USA). All the experiments were taken at room temperature.

Electrospinning of fibers

The electrospinning device (NS24, Inovenso, Turkey) was used for stating the electrospinning setup. In this technique, the polymer was dissolved in a suitable solvent and put in a syringe (10-ml plastic syringe) with a small hole at its end. The pump, which was located at the back of the syringe brings the polymer solution in the syringe into a continuous pressure field, that will push the tip across the pipette. The circular picker was placed 15 cm away from the needlepoint. Thereafter, the tension was applied between collector plates opposite the opening end of the polymer solution syringe. When the flow rate of the syringe pump is 2 mL /h and the applied voltage, which reaches 28-32 kV, the polymer drip changes from shape to a cone. The polymer solution, which does not have any surface tension, flows through the specially designed and very thin jet stream to the grounded target placed against the array. The fibers accumulated in the form of fiber rays on the grounded surface are constantly drawn and fibers are formed. All experiments took 3-4 hours and were performed in the room.

Table-1: Table of contents and physical characterization of produced solution samples.

Sample no.	Concentration of the Polymers	Density (g/cm^3)	Electrical Conductivity (µS/cm)	Surface Tension (mN/m)	Viscosity (mPa.s)
s1	10 wt. % PLA 3 wt. % Tween 80	1.45	1.8	28.69	623
s2	10 wt. % PLA 3 wt. % Tween 80 1 wt.% HSP	1.46	1.7	27.68	1096
s3	10wt. % PLA 3 wt. % Tween 80 2 wt.% HSP	1.51	1.6	26.78	1260
s4	10 wt. % PLA 3 wt. % Tween 80 3 wt.% HSP	1.52	1.3	25.49	1536

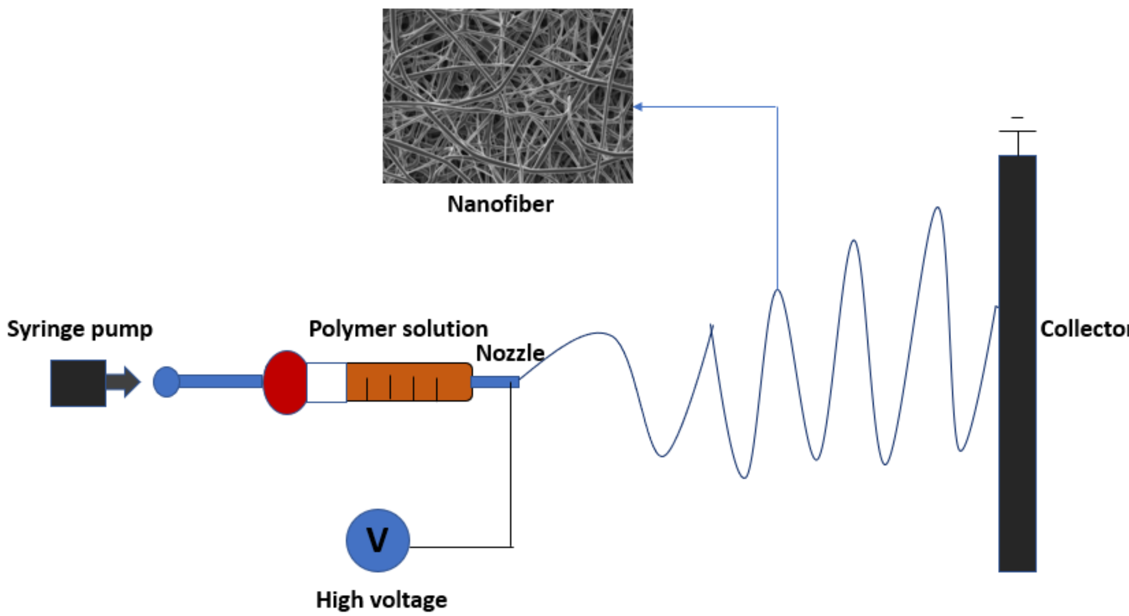

Fig. 1: Fiber production by using the electrospinning method.

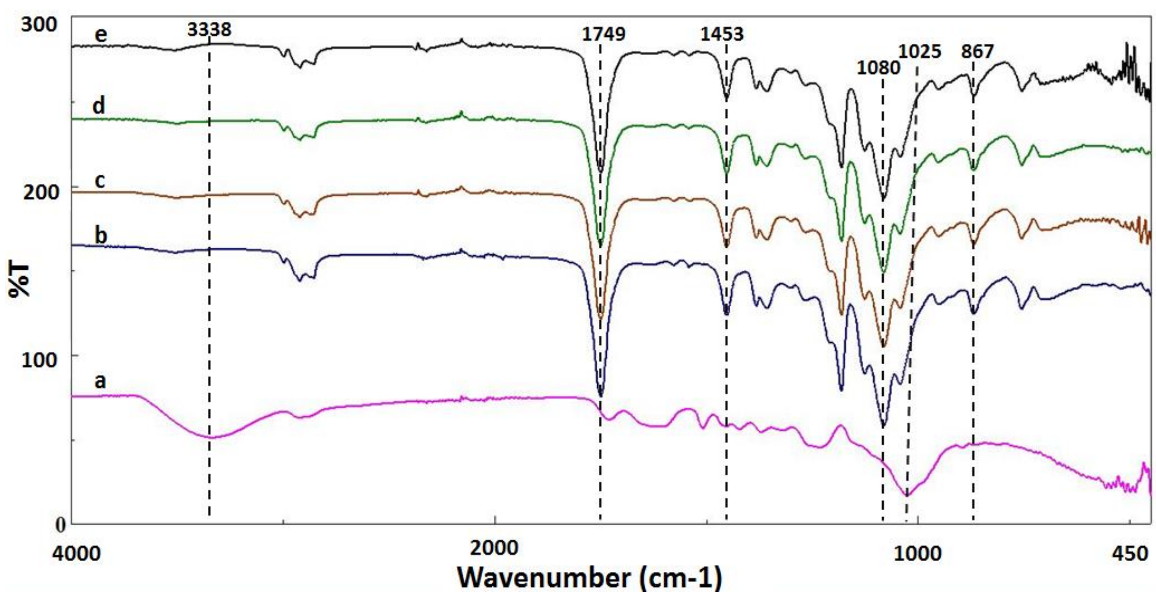

Fig. 2: FTIR spectrums of a) pure hazelnut shell powder, b) s1, c) s2, d) s3, and e) s4.

Characterization of the fabricated fibers

A scanning electron microscope (SEM) (EVO, ZEISS) was used for observing morphological characterization. Before imaging, the fibers were sputter-coated with gold-palladium for 120 seconds using a Quorum SC7620 Mini Sputter coater. The applied acceleration voltage was 10 kV. The diameters and distributions were determined by using image software (Olympus AnalySIS, USA). Fourier-transformed infrared (FT-IR) (Jasco, FT/IR 4700) was used for analyzing the molecular contents of the fibers. Measurements were made at a scanning range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1}. The tensile strength of the fiber samples was determined and evaluated by tensile strength measurement device (Instron 4411, MA, USA) ambient room temperature (23ºC). Tensile tests of the 3 samples were made for each ratio with the fibers, which were obtained from the solutions prepared in 4 different ratios. All fiber pieces were analyzed and the thicknesses of each sample were measured using micrometers (Mitutoyo MTI, USA). Four rectangular-shaped (1 × 5 cm) specimens were arranged for each pattern, and they were subjected to a tensile test with 5 mm /min^{-1} test speed and 1cm distance.

Results and discussion

They are many parameters that affect the electrospinning process, which are the physical properties of the solutions. Fiber formation and electrospun polymer fiber homogeneity are affected by these parameters. Solution electrical conductivity and viscosity affect fiber morphology and diameter, spinnability of the solution [6]. Table 1 shows the sample contents and their physical characterizations such as surface tension, viscosity, electrical conductivity, density measurement. As seen in Table 1, it was observed, that density was increased, when distinct percentages of HSP were added into the pure PLA solution. It has been observed in previous studies that hazelnut shell powder (HSP) increases density [7]. In addition, when different percentages of HSP were added to the pure PLA solution, the viscosity increased from 623 to 1536 mPa.s. Surface tension and electrical conductivity decreased as the amount of HSP increased. Fig. 2 indicates the FT-IR spectra of the fibers produced at different concentrations. Characteristic peaks of PLA were observed C=O vibration peak at 1749 cm^{-1}, CH_3 asymmetrical scissoring at 1453 cm^{-1}, C–O, C–O–C stretching at 1080 cm^{-1}, C–CH_3 stretching at 1042 $cm^{-1,}$ and C–COO stretching peak at 867 cm^{-1} [8]. The FT-IR spectrum of Hazelnut shell powder presented prominent absorption bands at 3338 cm^{-1}, 2919 cm^{-1}, 1025 cm-1 [9]. PLA indicates sharp peaks due to the small amount of hazelnut shell powder in the PLA/HSP composites.

SEM images and fiber size of the fiber samples were stated in Fig 3. As seen as all of the fibers were bead-free, smooth, and randomly oriented. The diameter distribution of these fibers was observed at 2092 µm without hazelnut shell powder. HSP was added to the composites (ϕ=2379, 64±635, 268 µm for b; ϕ=25581000, 339±, 806 µm for c; ϕ=2619, 24±967, 364µm) and diameters were increased. This result had shown, that by increasing the HSP proportion in the PLA/HSP solution, the average diameters of the fibers were increased. Hazelnut shell powder (HSP) was distributed homogeneously in the fiber structure.

Tensile test results of the four samples demonstrate the mechanical properties of the fiber samples were shown in Fig 4. With the amounts of Hazelnut shell powder was increased, the tensile strength of fiber was decreased from 2.3 MPa to 1.2 MPa. It is thought that a significant reason for the decrease is the lack of bonding between lignocellulosic fillers and polymer matrix [10, 11]. Strain at break values changed between 80-100%. Young's modulus ranged from 8.3 to 3.80 MPa. When the HSP concentration increased, increases in fiber diameter and distribution were observed. Thus, the mechanical properties of fibers with larger diameters decreased.

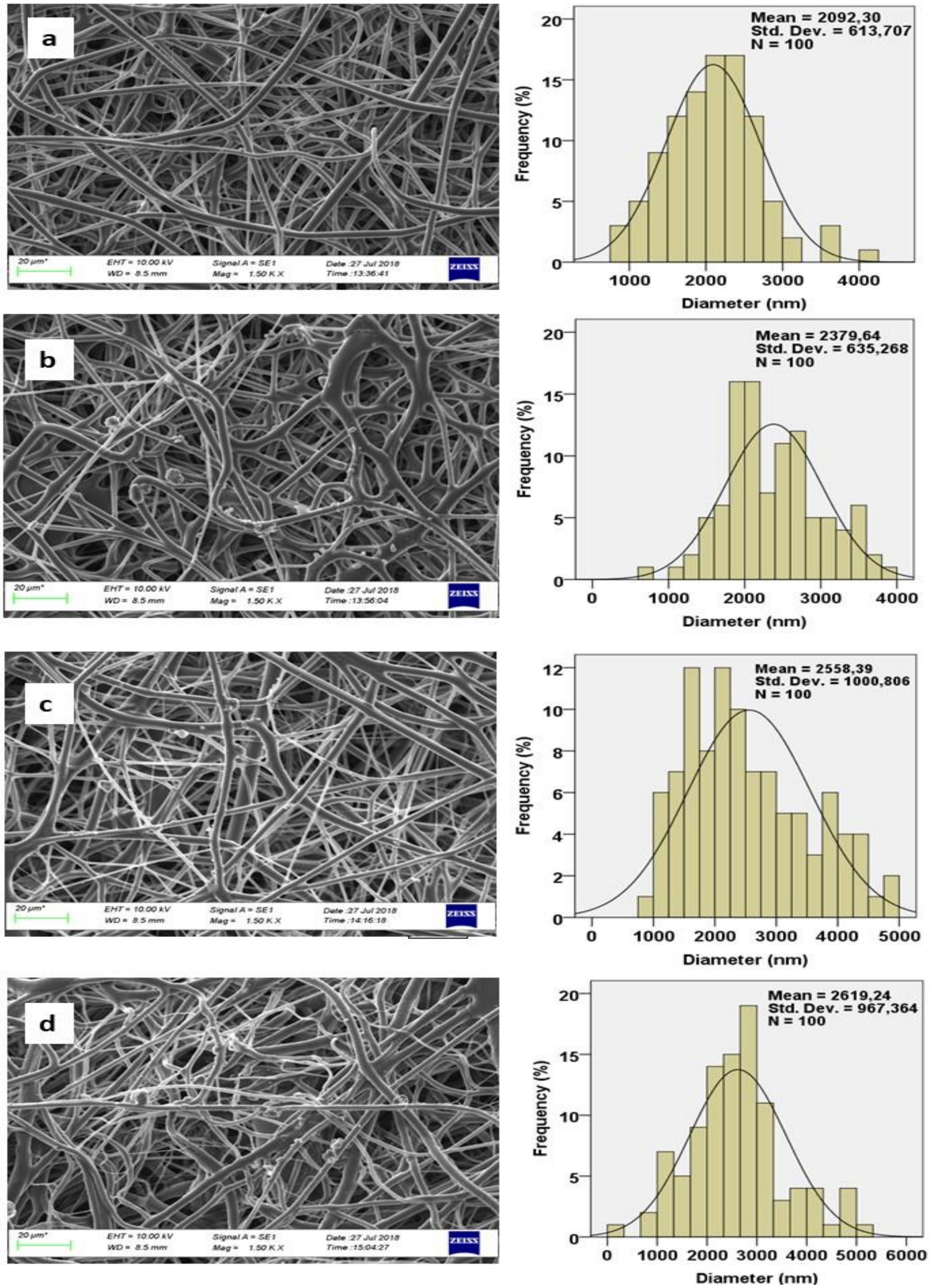

Fig. 3: SEM images and fiber diameter distribution of the composites. (a) s1, (b) s2, (c) s3, (d) s4.

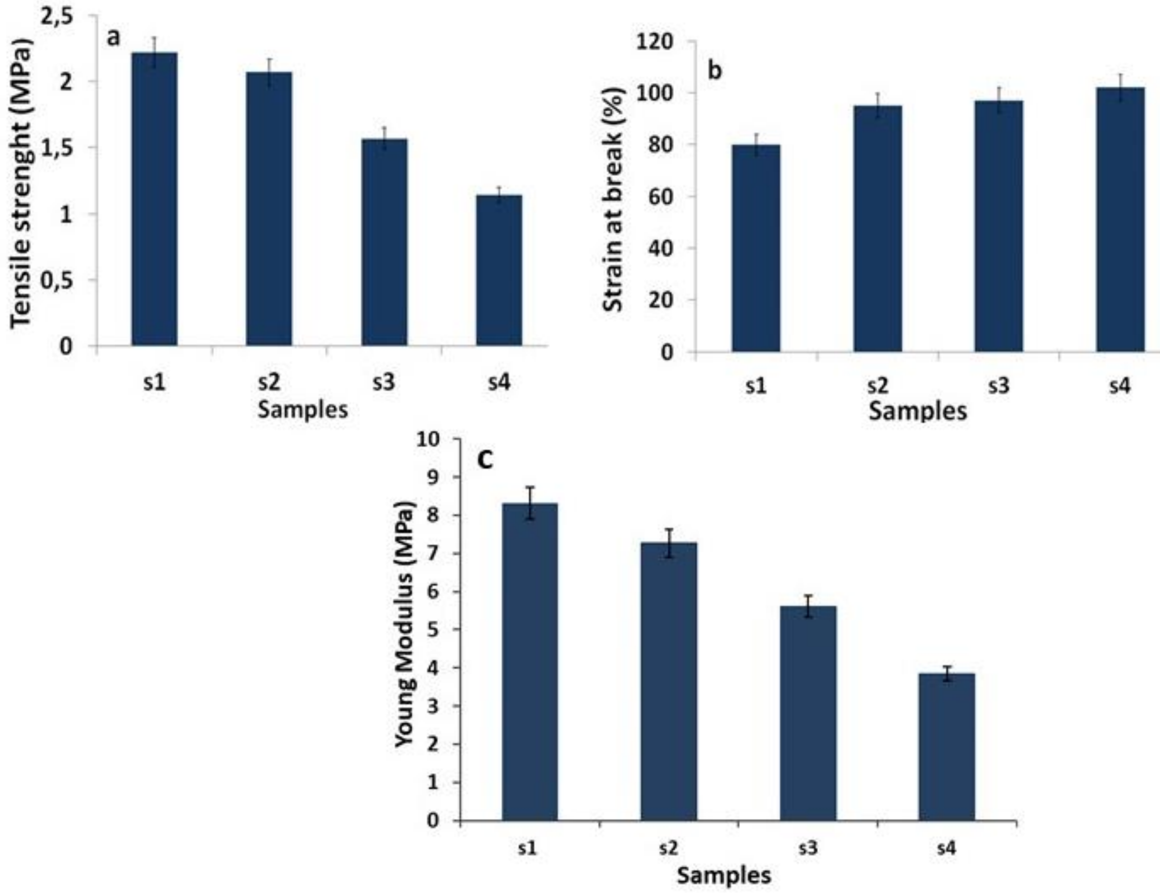

Fig. 4: (a) Tensile strength, (b) strain at break, and (c) young modulus of the composites.

Conclusion

In summary, fibers were obtained by adding hazelnut shell powders at different concentrations into Poly (lactic acid) (PLA) by using the electrospinning method. The results obtained from this study, electrospun fibers occur beatless. The addition of the hazelnut shell powder increased the size of electrospun fiber diameters. The tensile strength of the fibers decreased between the s1-s4 specimens. It has been shown that the tensile strength decreases as the diameter increases. However, the properties were negative compared to pure PLA at all rates. Therefore, the hazelnut powder additive did not show any improvement.

Acknowledgments

This study is funded by Marmara University with the BAPKO project (FEN-C-YLP-110718-0401).

References

1. M.O. Aydogdu, N. Ekren, M. Suleymanoglu, S. Erdem-Kuruca, C.C. Lin, E. Bulbul, M.N. Erdol, F.N. Oktar, U.K. Terzi, O. Kilic, O. Gunduz, Novel Electrospun Polycaprolactone/Graphene Oxide/Fe3O4 Nanocomposites for Biomedical Applications, *Colloids and Surfaces B: Biointerfaces* (2018)
2. G. Avsar, D. Agirbasli, M.A. Agirbasli, O. Gunduz, E.T. Oner. Levan based Fibrous Scaffolds Electrospun via Co-axial and Single-Needle Techniques for Tissue Engineering Applications. Carbohydrate Polymers (2018)
3. O. Avinc, A. Khoddami. Overview of poly(lactic acid) (PLA) fibre. *Fibre Chem*. (2009)
4. R. Bodîrlău, I. Spiridon, C.A. Teacă, Influence of components ratio upon mechanical properties of wood/thermoplastic polymer composites. *Rev Cellulose Chem. Technol*. (2009)
5. K.A. Iyer, J.M. Torkelson. Green composites of polypropylene and eggshell: Effective biofiller size reduction and dispersion by single-step processing with solid-state shear pulverization. *Compos Sci Technol*. (2014)
6. R. Konwarh, N. Karak, M. Misra. Electrospun cellulose acetate nanofibers: The present status

and gamut of biotechnological applications. *Biotechnology Advances*. (2013)

7. K. Karakus, İ. H. Basboga, İ. Atar, F. Mengeloglu, Utilization of hazelnut shells as filler in LDPE /PP based polymer composites, *Pro. Ligno*. (2017).
8. S. Cesur, F.N. Oktar, N. Ekren, et al. Preparation and characterization of electrospun polylactic acid/sodium alginate/orange oyster shell composite nanofiber for biomedical application. *J Aust Ceram Soc*. (2019)
9. Z. Gökdai, A. Sinağ, T. Yumak, Comparison of the catalytic efficiency of synthesized nano tin oxide particles and various catalysts for the pyrolysis of hazelnut shell. *Biomass and Bioenergy*. (2010).
10. A. Donmez Cavdar, F. Mengeloglu, K. Karakus, Effect of boric acid and borax on mechanical, fire and thermal properties of wood flour filled high density polyethylene composites. *Meas J Int Meas Confed*. (2015).
11. F Mengeloglu, K. Karakus, Thermal degradation, mechanical properties and morphology of wheat straw flour filled recycled thermoplastic composites. *Sensors*. (2008)