TEKSTİL VE MÜHENDİS

(Journal of Textiles and Engineer)

http://www.tekstilvemuhendis.org.tr

POLİKAKTİT ESASLI NANOLİF pH İNDİKATÖRLERİNİN TASARIMI VE GELİŞTİRİLMESİ

DESIGN AND DEVELOPMENT OF POLYLACTIDE BASED NANOFIBROUS pH INDICATOR

Handan PALAK*, Burçak KARAGÜZEL KAYAOĞLU

İstanbul Technical University, Textile Engineering Dept., İstanbul, Turkey

Online Erişime Açıldığı Tarih (Available online):30 Aralık 2022 (30 December 2022)

Bu makaleye atıf yapmak için (To cite this article):

Handan PALAK, Burçak KARAGÜZEL KAYAOĞLU (2022): Design and Development of Polylactide Based Nanofibrous Ph Indicator, Tekstil ve Mühendis, 29:128, 286-290.

For online version of the article: https://doi.org/10.7216/teksmuh.1222518

Araştırma Makalesi / Research Article

DESIGN AND DEVELOPMENT OF POLYLACTIDE BASED NANOFIBROUS pH INDICATOR

Handan PALAK[1*]
Burçak KARAGÜZEL KAYAOĞLU[1]

[1]İstanbul Technical University, Textile Engineering Dept., İstanbul, Turkey

Gönderilme Tarihi / Received: 01.09.2022
Kabul Tarihi / Accepted: 01.12.2022

ABSTRACT: In this study, a colorimetric pH indicator was developed using nanofibrous mats of polylactide (PLA) including turmeric, a natural dye. Firstly, nanofibrous mats were produced by dissolving PLA at different concentrations in chloroform (CHL)/dimethylformamide (DMF) at various volume ratios, and morphological analysis was performed. Subsequently, turmeric was added at a concentration of 2% wt. to the polymer solution having a PLA concentration of 10% in 75/25 CHL/DMF, and nanofibrous pH indicators were produced. Then, pH indicators containing turmeric were immersed into pH buffer solutions (pH 1, 4, 7 and 10), and color variations were measured using a spectrophotometer. It was foreseen that the produced pH indicators have the potential to be used in intelligent food packaging applications.

Key words: PLA, turmeric, nanofiber, electrospinning, pH indicator

POLİKAKTİT ESASLI NANOLİF pH İNDİKATÖRLERİNİN TASARIMI VE GELİŞTİRİLMESİ

ÖZ: Bu çalışmada, doğal bir boyarmadde olan turmerik içeren, polilaktit (PLA) esaslı nanolif yüzeyler kullanılarak kolorimetrik pH indikatörü geliştirilmiştir. Öncelikle, farklı konsantrasyonlarda PLA polimeri, çeşitli hacim oranlarında kloroform (CHL)/dimetilformamid (DMF) içerisinde çözdürülüp, elde edilen karışımlarla elektroeğirme yöntemi ile nanolif yüzeyler üretilmiş ve morfolojik analizler gerçekleştirilmiştir. Ardından, ağırlıkça %2 oranında turmerik, %10 PLA konsantrasyonuna sahip 75/25 CHL/DMF çözeltisi içerisine ilave edildikten sonra bu karışımdan nanolifli pH indikatörü üretilmiştir. Turmerik içeren bu pH indikatörlü, pH tampon çözeltilerine daldırılarak, spektrofotometrede renk değişimleri ölçülmüştür. Üretilen pH indikatörlerinin, akıllı gıda paketlemelerinde potansiyel olarak kullanılabileceği öngörülmüştür.

Anahtar Kelimeler: PLA, turmerik, nanolif, elektroeğirme, pH indikatörü

Sorumlu Yazarlar/Corresponding Author: *palakh@itu.edu.tr*
DOI: *https://doi.org/10.7216/teksmuh.1222518* *www.tekstilvemuhendis.org.tr*

This study was presented at "3rd International Congress of Innovative Textiles (ICONTEX2022)", May 18-19, 2022 Çorlu, Turkey. Peer review procedure of the Journal was also carried out for the selected papers before publication.

1. INTRODUCTION

The need of using sustainable and biobased polymers increases globally due to environmental concerns. PLA is a biobased, biodegradable and biocompatible aliphatic polyester, which is derived from renewable resources, i.e., corn starch and sugar cane. Due to its good mechanical and thermal properties, PLA is used in various engineering applications instead of petroleum-based polymers i.e., polyethylene terephthalate (PET) and polystyrene (PS) [1, 2]. PLA is a suitable polymer to be processed in different production methods such as single and twin screw extrusion, blown film extrusion, solution casting, and electrospinning.

Electrospinning is a practical technique to fabricate ultrafine polymer fibers in different diameters ranging from nanometers to micrometers by applying an electric field on the polymer solution. This technique is also convenient to incorporate various compounds i.e., dyestuff, nanoparticles, antioxidants, antimicrobials and drugs, into the polymer solution to develop nanofibrous mats with improved properties. In addition, electrospun nanofibers have outstanding properties such as high porosity, small pore size, and a very high surface area to volume ratio [3]. Accordingly, electrospun PLA nanofibers show great potential in tissue engineering [4], drug delivery [5], filtration [6], sensor application [7], and food packaging [8].

Intelligent food packaging has emerged due to growing consumer concerns about food quality. In these packaging systems, gas sensors, time-temperature indicators and pH indicators are used [9]. During the deterioration of food, pH of the medium changes. A pH indicator is able to sense changes in the pH and warns the consumers visually by changing its color. These indicators include a pH-sensitive dye and a matrix that immobilizes the dye [10]. For this purpose synthetic dyes such as bromocresol purple, bromothymol blue, and methyl red can be used [11, 12]. However, pH-sensitive synthetic dyes have harmful effects on the human health since they are toxic and allergenic [13]. For this reason, dyes from natural resources have become remarkable in recent years. On the other hand, since nanofibrous mats respond to functionalization faster than polymer films due to their high surface area [14], they are appropriate materials to be used as a matrix in the development of a pH indicator.

The main goal of this study was to investigate the electrospinning behavior of PLA and develop PLA-based nanofibrous mats. Subsequently, the polymer solution, resulting in good fiber morphology, was chosen and a natural dye, turmeric, was added, and an environmentally friendly nanofibrous colorimetric pH indicator was developed for potential use in intelligent food packaging applications.

2. MATERIALS AND METHODS

2.1 Materials

Commercial grade of PLA (4060D), which is amorphous with D-lactide content of 12 mol% and has a molecular weight of 190 kg/mol, was supplied from NatureWorks LLC (USA). CHL (99% purity, Sigma-Aldrich) and DMF (99% purity, Sigma-Aldrich) and were used as solvents. Turmeric, a natural dye, was supplied from GemmaNatural (Turkey). pH buffer solutions (pH 1, 4, 7 and 10) were supplied from ISOLAB Chemicals (Turkey).

2.2 Sample preparation

The polymer solutions were prepared by dissolving PLA, with three different polymer concentrations (5, 7.5, and 10 %wt.), in CHL/DMF (C%-D%) solvent blend at different volume ratios 100-0, 75-25, 50-50, 25-75, 0-100 v/v %) for 4h at 50°C. Turmeric (2% wt.) was added to the PLA polymer solution, having a concentration of 10% in 75/25 CHL/DMF, and the final solution was magnetically stirred for 20h at room temperature.

An electrospinning device of Inovenso Nanospinner24 (Turkey) was used to produce electrospun nanofibrous mats. The applied voltage was in the range of 10-15 kV and tip-to-collector distance and feed rate were fixed at 15-17 cm and 1-1.5 ml/h, respectively.

2.3 Methods

The morphology of electrospun mats was investigated by a Tescan Vega3 scanning electron microscope (SEM). Before imaging, samples were cut into a size of 1cm x 1cm and mounted on a stub and placed into a Quorum Sputter Coater to be coated with a thin layer of Au/Pd for 165 seconds. To measure the diameter of the nanofibers, SEM images at high magnification (5kX) were analyzed with ImageJ software. 100 measurements were taken on each sample, and average nanofiber diameters were calculated.

The nanofibrous indicators were cut in a size of 20 × 20 mm and immersed in each pH buffer solutions. The colors of the pH indicators were determined using a Datacolor 3890 spectrophotometer. The values of L* (brightness), a* (red/green) and b* (yellow/blue) were measured, and the mean values of L*, a* and b* were used to calculate the total color difference (ΔE) with Equation (2) [10].

$$\Delta L^* = L - L_0;\ \Delta a^* = a - a_0;\ \Delta b^* = b - b_0 \tag{1}$$

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

It was observed that none of the solutions with 5 wt% PLA concentration produced fibers since the number of entanglements in the polymer solutions was inadequate.

When the polymer concentration increased to 7.5 wt %, beads were observed in SEM images (Figure 1) almost at each solvent ratio. It was concluded that bead formation was unavoidable due to inherent amorphous structure and low polymer concentration. On the other hand, since the dielectric constant of DMF is higher than that of CHL, the polymer jet carries more free charge and stretches more under an electric field [15]. In addition, DMF has a high boiling point, which increases the solvent evaporation time and provides the polymer jet with sufficient time for stretching [16]. Thus, when the DMF content increased, the fiber diameter noticeably decreased.

When the polymer concentration increased from 7.5 to 10 wt%, less beaded fibers were observed (Figure 2). In 100% CHL, microfibers, having an average fiber diameter of 8.4 ± 2 µm, were produced due to the low dielectric constant of CHL. Moreover, the use of 100% CHL was not efficient since the high volatility of CHL caused needle-clogging. With the addition of 25% v/v DMF, the mean fiber diameter decreased from micro-scale to nano-scale, 378 ± 61 nm, and the problem of needle-clogging was eliminated [17]. Accordingly, the polymer solution having a concentration of 10 wt% in 75/25% CHL/DMF was chosen to add turmeric for the purpose of developing PLA based nanofibrous colorimetric pH indicator.

The SEM image of the nanofibrous pH indicator (Figure 3) showed that turmeric was dispersed in the polymer solution successfully since no beads were observed. The average fiber diameter was measured as 765±78 nm, which was larger compared to the nanofibers without turmeric as a result of the increased concentration of the polymer solution.

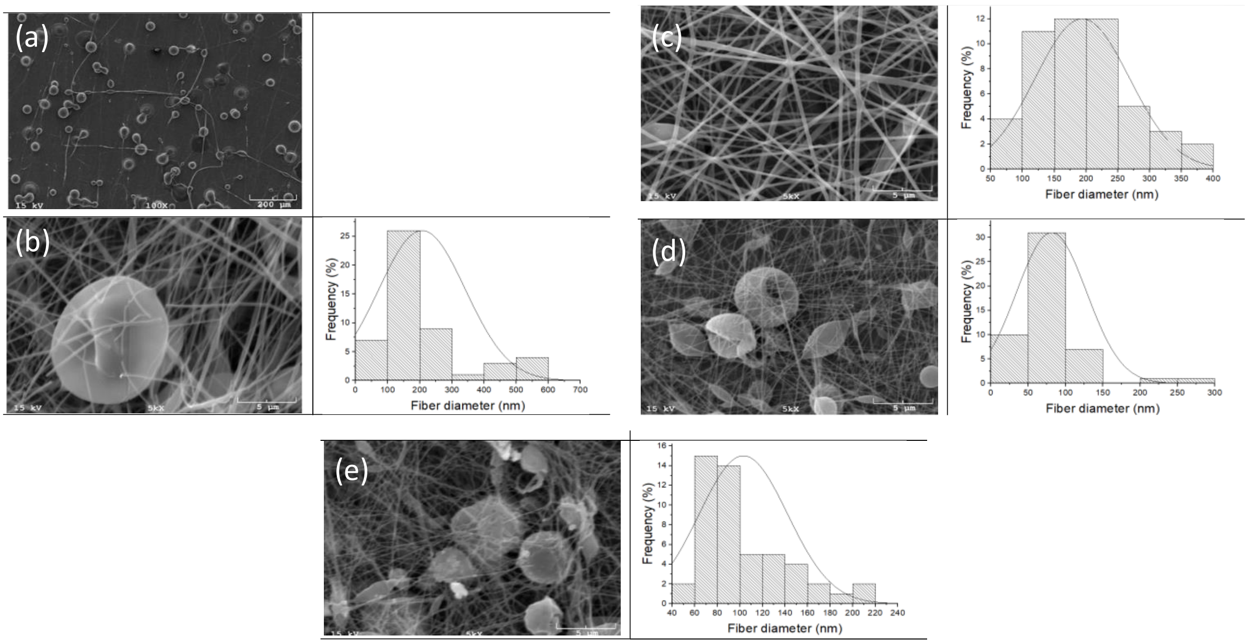

Figure 1. SEM images and fiber diameter distribution of 7.5 wt% PLA at various solvent concentrations. (a) C100-D0, (b) C75-D25, (c) C50-D50, (d) C25-D75, (e) C0-D100.

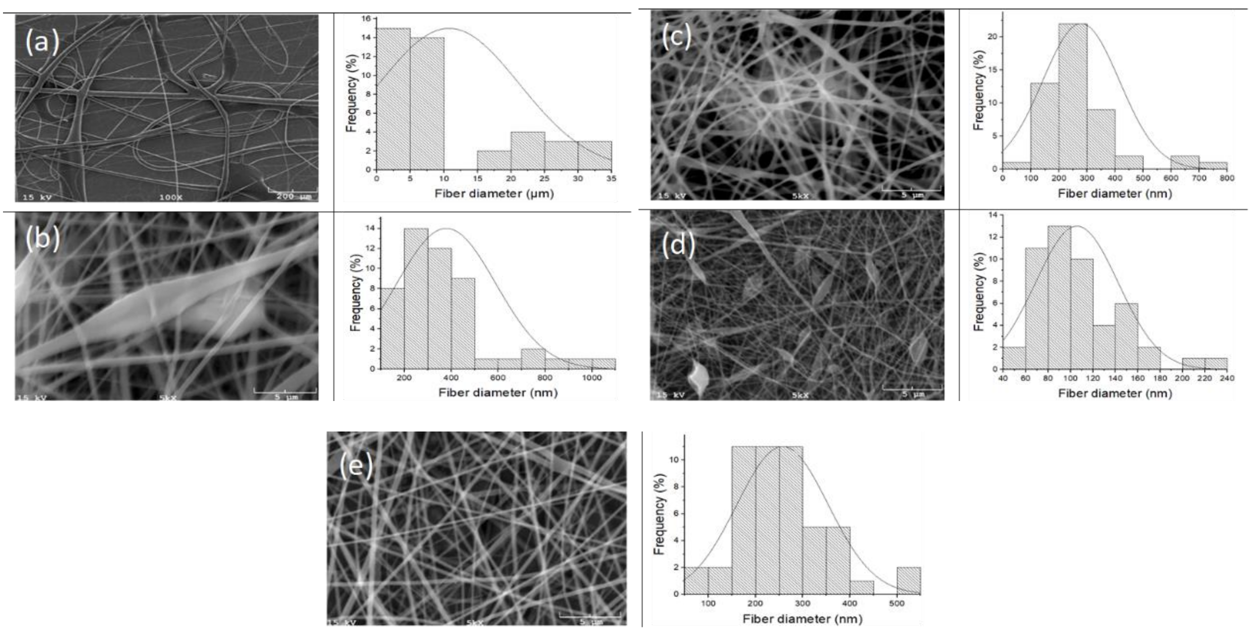

Figure 2. SEM images and fiber diameter distribution of 10 wt% PLA at various solvent concentrations. (a) C100-D0, (b) C75-D25, (c) C50-D50, (d) C25-D75, (e) C0-D100.

3.2. Color analysis

The color change of nanofibrous indicators in different pH buffer solutions was shown in Figure 3. ΔE values of pH indicators (Table 1) were calculated from L*, a* and b* values (Table 2). It was previously reported that a ΔE higher than 5 indicates a change in color that is perceptible by the human eye, and a ΔE higher than 12 indicates an absolute difference in color [18, 19]. Accordingly, the nanofibrous pH indicators developed in the present study are promising for the visual evaluation of pH change with ΔE values higher than 5. On the other hand, a major color variation was observed at pH 10, similar to previous studies [20, 21].

4. CONCLUSION

In this study, colorimetric pH indicators were developed using PLA based nanofibrous mats including turmeric. First of all, morphological analysis was performed on nanofibrous mats produced at different polymer concentrations and solvent ratios. When the polymer concentration increased from 7.5 to 10 wt%, less beaded fibers were observed. In 100% CHL, microfibers were produced due to the low dielectric constant of CHL. In addition, the high volatility of CHL caused needle-clogging.

With the addition of 25% v/v DMF, the mean fiber diameter decreased to nano-scale, and the problem of needle-clogging was solved. ΔE of the nanofibrous indicators in pH buffer solutions were higher than 5, and a major color variation (ΔE>12) was observed at pH 10. Therefore, the proposed indicators, showing reliable responses to pH variations, can be applied in intelligent food packaging and contribute to improving food safety.

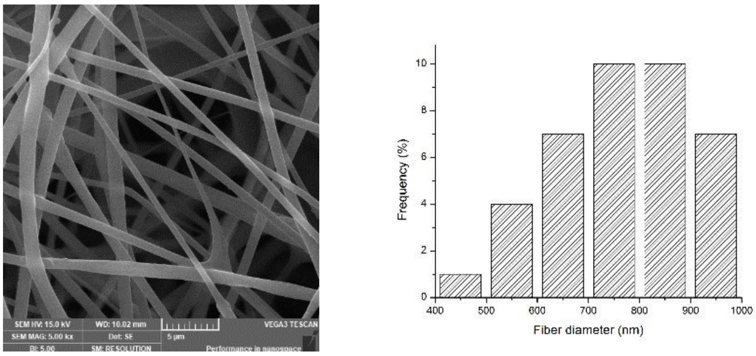

Figure 3. SEM image and fiber diameter distribution of nanofibrous pH indicator including 10 wt% PLA and 2% wt. turmeric at a solvent concentration of C75-D25.

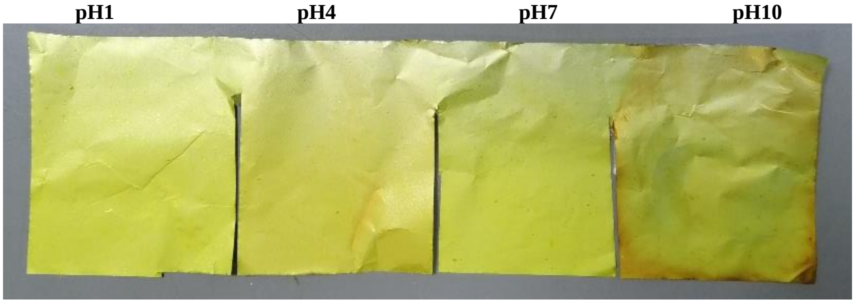

Figure 3. Color change of nanofibrous pH indicators in different pH buffer solutions.

Table 1. ΔE values of pH indicators at pH 1, 4, 7 and 10.

pH	**4**	**7**	**10**
1	8.38±0.42	6.63±0.35	19.18±0.28
4		6.38±0.31	12.13±0.57
7			13.42±0.68

Table 2. L*, a*, b* values of pH indicators at pH 1, 4, 7 and 10.

pH	**1**	**4**	**7**	**10**
L*	90.50	87.35	90.87	86.00
a*	-20.70	-15.22	-20.43	-14.31
b*	76.78	71.28	70.17	59.26

REFERENCES

1. Auras, R., Harte, B., and Selke, S., (2004), *An overview of polylactides as packaging materials*, Macromol Biosci, 4, 835-864.
2. Nofar, M., Maani, A., Sojoudi, H., et al, (2015), *Interfacial and rheological properties of PLA/PBAT and PLA/PBSA blends and their morphological stability under shear flow*, Journal of Rheology, 59(2), 317–333.
3. Subbiah, T., Bhat, G.S., Tock, R.W., et al, (2005), *Electrospinning of nanofibers*, J. Appl. Polym. Sci, 96, 557-569.
4. Hwang, T.I., Maharjan, B., Tiwari, A.P., et al, (2008), *Facile fabrication of spongy nanofibrous scaffold for tissue engineering applications*, Mater. Lett, 219, 119–122.
5. Scaffaro, R., Maio, A. and Lopresti, F., (2019), *Effect of graphene and fabrication technique on the release kinetics of carvacrol from polylactic acid,* Compos Sci Technol, 169, 60–69.
6. Li, L., Hashaikeh, R., and Arafat, H.A., (2013), *Development of eco-efficient micro-porous membranes via electrospinning and annealing of poly(lactic acid),* J. Membr. Sci 2013; 436: 57–67.
7. Aliheidari, N., Aliahmad, N., Agarwal, M., et al., (2019), *Electrospun nanofibers for label-free sensor applications,* Sensors, 19(16), 3587.
8. Aydogdu, A., Yildiz, E., Ayhan, Z., et al., (2019), *Nanostructured poly(lactic acid)/soy protein/HPMC films by electrospinning for potential applications in food industry,* Eur. Polym. J, 112, 477–486.
9. Fuertes, G., Soto, I., Carrasco, R., et al., (2016), *Intelligent packaging systems: sensors and nanosensors to monitor food quality and safety,* Journal of Sensors, doi: 10.1155/ 2016/ 4046061.
10. Kuntzler, S.G., Costa, J.A.V., Brizio, A.P.D.R., et al., (2020), *Development of a colorimetric pH indicator using nano fibers containing,* Food Chemistry, 328, 126768.
11. Chen, H., Zhang, M., Bhandari, B., et al., (2019), *Development of a novel colorimetric food package label for monitoring lean pork freshness,* LWT - Food Science and Technology, 99,43–49.
12. Siripongpreda, T., Siralertmukul, K., Rodthongkum, N., (2020), *Colorimetric sensor and LDI-MS detection of biogenic amines in food spoilage based on porous PLA and graphene oxide,* Food Chemistry, 329, 127165.
13. Devarayan, K., Kim, B.S., (2015), *Reversible and universal pH sensing cellulose nanofibers for health monito,* Sensors and Actuators B, 209,281–286.
14. Jorge, B.C. De, and Gross, J., (2020). “Smart nanotextiles for application in sustainable agriculture”. “*Nanosensors and nanodevices for smart multifunctional textiles*”, Elsevier.
15. Jarusuwannapoom, T., Hongrojjanawiwat, W., Jitjaicham, S., et al. (2005), *Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers,* Eur. Polym. J, 41, 409-421.
16. McCullen, S., Stano, K.L., Derrick, S., et al., (2007), *Development, optimization, and characterization of electrospun poly(lactic acid) nanofibers containing multi-walled carbon nanotubes*, J. Appl. Polym. Sci, 105, 1668-1678.
17. Palak, H., Güler, E., Nofar, M., and Kayaoglu, B.K., (2022), *Effects of D-lactide content and molecular weight on the morphological, thermal, and mechanical properties of electrospun nanofiber polylactide mats*, Journal of Industrial Textiles, doi: 10.1177/15280837221090260.
18. Tassanawat, S., Phandee, A., Magaraphan, R., et al.,(2007), *pH-sensitive PP/clay nanocomposites for beverage smart packaging,* Proceedings of the 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems, pp. 16–99.
19. Barba, F,J,, Esteve, M.J., and Frigola, A., (2013), *Physicochemical and nutritional characteristics of blueberry juice after high pressure processing.* Food Research International, 50, 545–549.
20. Zhai, X., Wang, X., Zhang, J., et al., (2020), *Extruded low density polyethylene-curcumin film: A hydrophobic ammonia sensor for intelligent food packaging,* Food Packaging and Shelf Life, 26, 100595.
21. Kuswandi, B., Larasati, T.S., Abdullah, A., et al., (2012), *Real-time monitoring of shrimp spoilage using on-package sticker sensor based on natural dye of curcumin,* Food Anal. Methods, 5, 881–889.