Polycaprolactone-Polydiacetylene Electrospun Fibers for Colorimetric Detection of Fake Gasoline

SHAMSHAD ALI*, FAROOQ AHMED**, AND AWAIS KHATRI**

RECEIVED ON 14.10.2015 ACCEPTED ON 14.12.2015

ABSTRACT

PCDA (Pentacosadiynoic Acid) monomers were successfully embedded in PCL (Poly ε-Caprolactone) polymer matrix by electrospinning process for the first time. The resultant EFM (Electrospun Fibers Mat) was photo-polymerized under 254 nm UV light that enables colorimetric detection of fake gasoline. Results revealed that the fake gasoline develops a red color mat within 5 sec. FE-SEM images showed that the fake gasoline treatment dissolved the PCL EFM that give access to interact with PDA polymer. The proposed litmus-type sensor based on PCL-PDA EFM is highly sensitive to fake gasoline and can be fabricated easily.

Key Words: Pentacosadiynoic Acid, Poly (å-Caprolactone), Electrospinning, Fake Gasoline, Red Color.

1. INTRODUCTION

Automobile gasoline is a product obtained through the fractional distillation of petroleum [1]. It is a complex mixture of organic compounds ranging from C_4-C_{12} carbon atoms [2]. The illicit addition of organic solvents in gasoline is carried out worldwide due to the sake of economic gains [3]. However, such a polluted gasoline can lead to a reduction of engine life time as well as an increased environmental load [4]. More significantly; such a malpractice results in a loss of huge amount of tax revenue. The aromatic hydrocarbons and aliphatic hydrocarbons (light and heavy) are most frequently added as an adulterant in the pure gasoline. The former causes a reduction of the gasoline departure from the engine while the later needs more energy to explode [2].Toluene is the most commonly used adulterant [5] and the addition of an excess amount of ethanol (>23%) in pure gasoline is practiced in Brazil due to the large difference in the prices of gasoline and ethanol [6]. Moreover, ethanol is cheap and miscible in gasoline. It is reported that the fake gasoline has been sold about 50% less price in comparison to the pure gasoline, and the composition of the adulterants used in the spurious gasoline include thinner, toluene and methanol [5].

Gasoline adulterants are easy to find in the markets and their detection is a difficult task since it requires the testing of a large number of samples to determine the hundreds of organic compounds present in the pure and fake or polluted gasoline [6].There are numerous test methods and instruments employed to detect the adulterants in gasoline including ASTM D 86 (Test method for distillation), ASTM D 381 (Test method for gum content),

* Assistant Professor, and **Associate Professor,
Department of Textile Engineering, Mehran University of Engineering & Technology, Jamshoro

ASTM D 482 (Test method for ash), ASTM D 4052 (Test method for density), Fourier transform infrared spectroscopy [6], flame emission spectroscopy [1] and gas chromatography [2]. However, these instruments are expensive, time taking and skilled personnel are required for data analysis and interpretation.

PDAs are a family of conjugated polymers, insoluble in most of the solvents [7]. They are generally prepared by the UV irradiation of self-assembled DA (Diacetylene) monomers, exhibiting a distinct blue color [8]. Under environmental stimulation, a chromatic shift occurs resulting in a blue-to-red color transition of PDA which can be observed visually [9]. Electrospinning has been proven an efficient method to produce polymer fibers with diameters in the range of 2nm to several micrometers [10]. It fabricates nanofibers with small pore structure, higher surface area and good interconnectivity amongst fibers [11]. In the last couple of years, the encapsulation of PDA polymer within electrospun fibers was investigated as a promising substrate for sensor applications including Lead ion recognition and chemosensor for α-cyclodextrin [5,12-14].

In the present study, a litmus-type sensor by embedding PDA polymer in PCL polymer matrix for the colorimetric identification of fake gasoline was prepared. PCL was chosen on account of its inherent properties including dissolution in toluene, biocompatibility and environmental degradability, as well as good mechanical properties [15-17]. To the best of our literature survey, no previous attempt were undertaken to use PCL as a potential substrate for detecting the fake gasoline.

2. EXPERIMENTAL

2.1 Materials

10,12-PCDA and PCL (M_n: 70,000-90,000) were purchased from Sigma-Aldrich, Co., USA. Toluene and methanol were obtained from Daejung Chemicals and Metals Co., Limited Korea. Thinner used in this study was of commercial grade. The commercial gasoline samples were taken from a filling station operated by GS Korea and used as-received unless otherwise indicated.

2.2 Preparation of Electrospun Fibers Based Sensor

Electrospinning set up with a high-voltage power supply (Nano NC, Korea) was used as the source of the electric field. A solution of PCL (9 wt.%) and PCDA (4 wt.%) in chloroform:dimethylformamide (9:1, w/w) was prepared. The polymer solution was stirred overnight under standard conditions (25°C temperature and 65% relative humidity) before electrospinning. The polymer solution was supplied through a 10 ml plastic syringe at a controlled feeding rate of 0.1 mL/h (Kd Scientific syringe pump) through a 23 G metal needle. Several parameters were applied in order to optimize the electrospinning of the polymer solution and the optimal parameters were chosen as follows. The voltage of 11 kV was applied and the tip-to-collector distance was fixed at 15 cm. Electrospun fibers were deposited continuously over the metallic drum for 30 min. The thickness of the mats was in between 20-30 μm; and was kept in the dark for a day before use.

Photo-polymerization of the PCDA embedded PCL EFMs were done by irradiation under 254 nm UV light (Spectroline ENF 260C/FE, USA) for 30-180 s. The samples were placed at a distance of 2 cm from the UV light source.

2.3 Sensor Test of Electrospun Fibers

The UV irradiated PCL-PDA EFM was placed on a glass dish containing 10 mL gasoline sample (commercial and fake) for 120s. The resulting color change of the mat in gasoline sample was recorded with a digital camera (Canon Powershot G12). Each sensor test was performed five times to observe the reproducibility.

2.4 Characterization

The morphology of electrospun fibers was studied under FE-SEM (JSM 6701F, JEOL Japan). All samples were sputtered with Platinum under vacuum before assessment.

3. RESULTS AND DISCUSSION

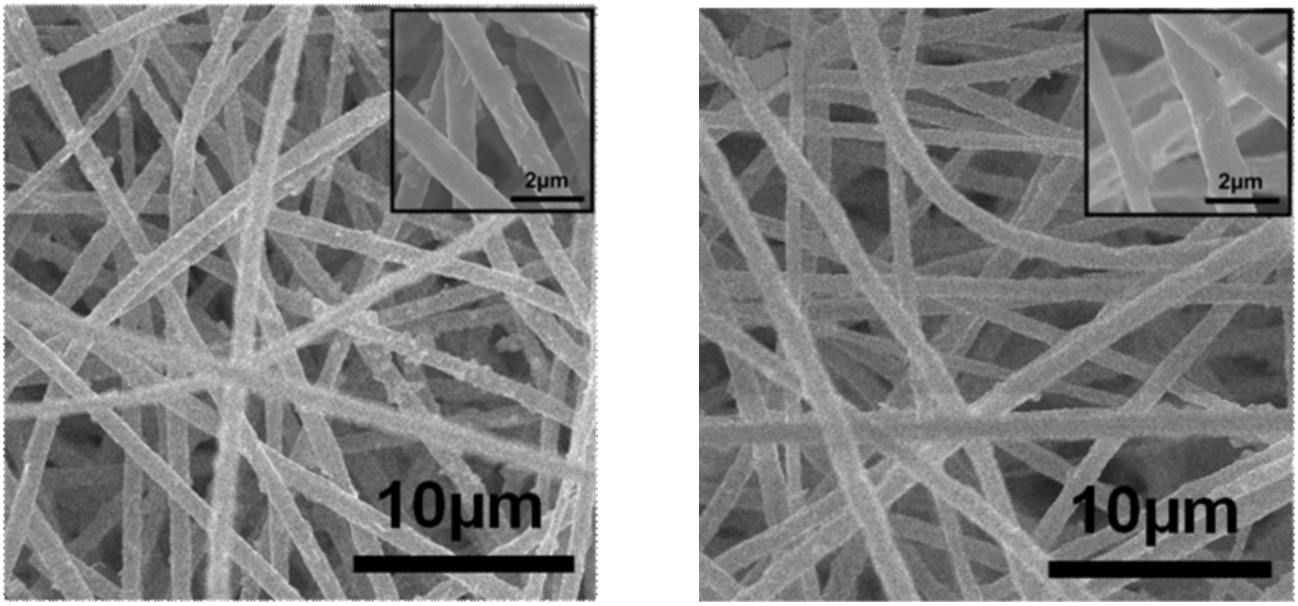
3.1 Morphology of Electrospun Fibers

The FE-SEM images of electrospun fibers are presented in (Fig. 1(a-b)). It can be seen from the images that the electrospun fibers are bead-free; and the size and shape of the individual fibers remained unaffected from the UV irradiation [8,13].

3.2 Sensor Test of Electrospun Fibers

The effect of UV irradiation time on PCL-PDA EFMs is shown in Fig. 2. A gradual increase in the depth of a blue color was observed by increasing UV irradiation time on PCL-PDA EFMs. It suggests that more inter-chain interaction occurs in between the neighboring PCDA monomer chains within the EFM to make PDA polymer- an insoluble polymer in common organic solvents. Furthermore, we observed that the blue color of the UV irradiated PCL-PDA EFMs remained unchanged after six months in the standard atmospheric conditions.

In order to explore the effect of UV irradiation time on proposed sensor system, we have chosen UV irradiated PCL-PDA EFM (30 s) and UV irradiated PCL-PDA EFM (180s) for further experiments.



(a) AS-SPUN *(b) 254 NM UV LIGHT IRRADIATED FOR 60S*

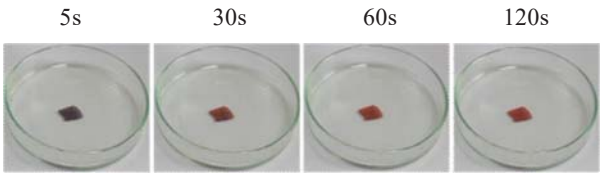
FIG. 1. FE-SEM IMAGES OF PCL-PDA ELECTROSPUN FIBERS

FIG. 2. PHOTOGRAPHS OF PCL-PDA EFMS AFTER EXPOSURE TO 254 NM UV IRRADIATION FOR DIFFERENT TIME DURATION (COLOURED FIG. IS AVAILABLE ONLY AT JOURNAL'S ONLINE ARCHIVES)

Fig. 3(a-b) demonstrates the color change of the PCL-PDA EFM after immersion in commercial gasoline for different time periods. It is obvious that the UV irradiated PCL-PDA EFM (30 s) displayed a blue-to-red color transition in commercial gasoline (Fig. 3(a)). This may be due to the dissolution of the un-polymerized residual solvatochromic PCDA monomers as well as partially polymerized oligomers in commercial gasoline, which leads to a partial distortion of the polymer backbone accompanied with a blue-to-red color transition [18]. On contrary, there was no color transition observed for UV irradiated PCL-PDA EFM (180s) when immersed in commercial gasoline (Fig. 3(b)).The probable reason may be due to the absence of the un-polymerized PCDA monomers and partially polymerized oligomers within the mat, which dissolved in commercial gasoline.This shows that the UV irradiation time is critical for the blue-to-red color transition of the PCL-PDA EFM incubated in commercial gasoline.

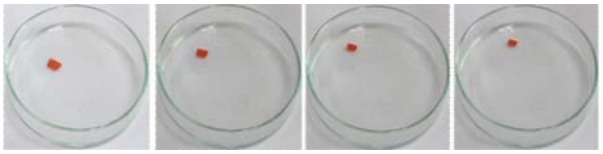
Fake gasoline was prepared in accordance to a previous report by mixing three different solvents, that is, thinner (60%), toluene (10%) and methanol (10%) [5]. Fig. 3(c-d) displayed the effect of fake gasoline treatment on the color change of PCL-PDA EFM for different time period. The UV irradiated PCL-PDA EFMs showed a blue-to-red color transition in fake gasoline (Fig. 3(c-d)). Significantly, dark red color was observed for UV irradiated PCL-PDA EFM (180s) in comparison to the UV irradiated PCL-PDA EFM (30s). The blue-to-red color change of the mats is very prominent and can easily be detected visually. It was also revealed that the red color of the mats remained unchanged after six months under standard atmospheric conditions. Moreover, we found that UV irradiated PCL-PDA EFM (180s) can provide us a clear distinction in between commercial gasoline and fake gasoline within a short time period (5s).

In order to comprehend the reasoning behind the color transition appeared with PCL-PDA EFM treated with fake gasoline, FE-SEM micrographs of the mats treated with commercial gasoline and fake gasoline were obtained (Fig. 4). Fig. 4(a)showed the smooth morphology of the electrospun fibers suggesting that commercial gasoline treatment did not damage the physical structure of the mat. On the other hand, fake gasoline treatment demonstrated the collapsed morphology of the electrospun fibers revealing the complete disappearance of the physical structure of the mat (Fig. 4(b)). Therefore, we found that fake gasoline treatment is responsible for the dissolution of the PCL electrospun fibers that brings about the blue-to-red color transition of the mat.

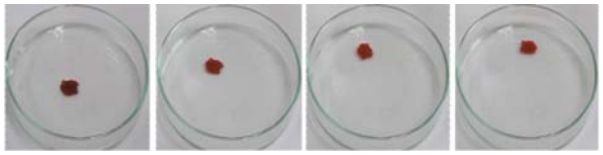


(a) UV IRRADIATION TIME OF 30s

(b) UV IRRADIATION TIME OF 180s, PHOTOGRAPHS OF UV IRRADIATED PCL-PDA EFMS AFTER EXPOSURE TO FAKE GASOLINE

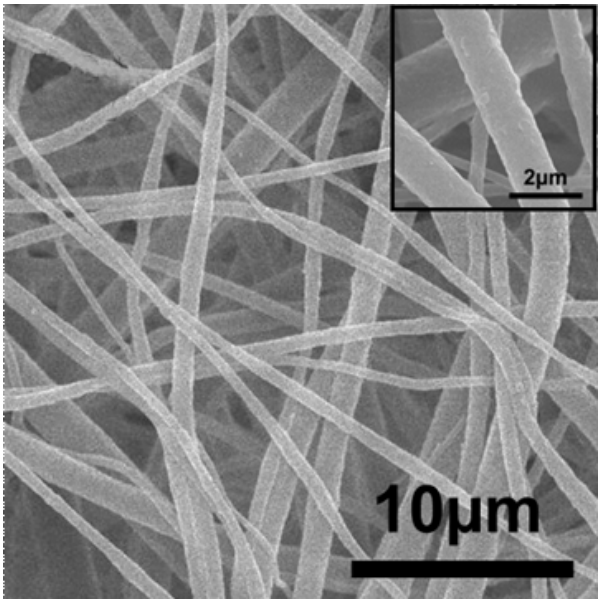


(c) UV IRRADIATION TIME OF 30s

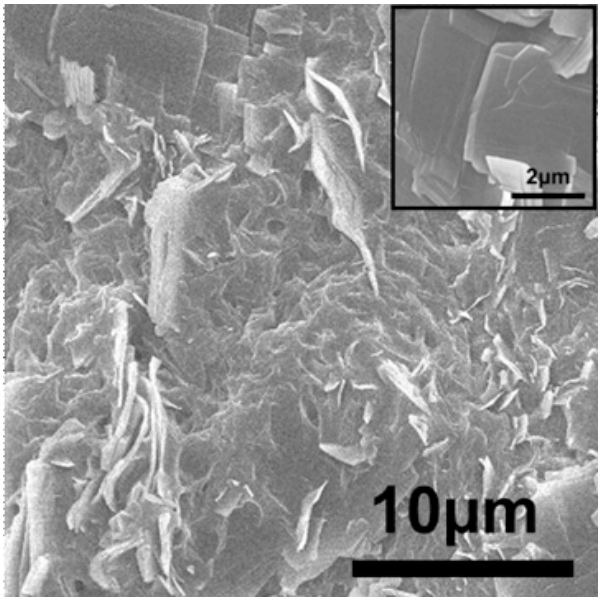


(d) UV IRRADIATION TIME OF 180s

FIG. 3. PHOTOGRAPHS OF UV IRRADIATED PCL-PDA EFMS AFTER EXPOSURE TO COMMERCIAL GASOLINE (COLOURED FIG. IS AVAILABLE ONLY AT JOURNAL'S ONLINE ARCHIVES)



(a) TREATED WITH COMMERCIAL GASOLINE



(b) TREATED WITH FAKE GASOLINE. THE UV IRRADIATION TIME WAS 180SFIG.

4. FE-SEM IMAGES OF UV IRRADIATED PCL-PDA ELECTROSPUN FIBERS

4. CONCLUSIONS

We successfully prepared sensor based on PDA-PCL EFM for the colorimetric detection of fake gasoline. Results showed that UV irradiated PCL-PDA EFM (180s) can provide a clear distinction in between commercial gasoline and fake gasoline. It gives a blue-to-red color transition within 5s when exposed to fake gasoline. FE-SEM images showed that the fake gasoline is responsible for the dissolution of PCL electrospun fibers that give access to interact with PDA polymer.

ACKNOWLEDGEMENTS

First author is grateful for the financial support received from Higher Education Commission Pakistan, under the HRDI-UESTPs/UETs scholarship and Mehran University of Engineering & Technology, Jamshoro, Pakistan.

REFERENCES

[1] de Paulo, J.M., Barros, J.E., and Barbeira, P.J., "Differentiation of Gasoline Samples Using Flame Emission Spectroscopy and Partial Least Squares Discriminate Analysis", Energy & Fuels, Volume 28, No. 7, pp. 4355-61, 2014.

[2] Wiedemann, L., d'Avila, L., and Azevedo, D., "Adulteration Detection of Brazilian Gasoline Samples by Statistical Analysis", Fuel, Volume 84, No. 4, pp. 467-73, 2005.

[3] Mendes, G., and Barbeira, P.J., "Detection and Quantification of Adulterants in Gasoline Using Distillation Curves and Multivariate Methods", Fuel, Volume 112, pp. 163-71, 2013.

[4] Wiziack, N., Catini, A., Santonico, M., D'amico, A., Paolesse, R., Paterno, L., Fonseca, F.J., and Natale, C.Di., "A Sensor array Based on Mass and Capacitance Transducers for the Detection of Adulterated Gasolines", Sensors and Actuators-B, Chemical, Volume 140, No. 2, pp. 508-13, 2009.

[5] Lee, J., Balakrishnan, S., Cho, J., Jeon, S-H., and Kim, J-M., "Detection of Adulterated Gasoline Using Colorimetric Organic Microfibers", Journal of Materials Chemistry, Volume 21, No. 8, pp. 2648-55, 2011.

[6] Teixeira, L.S., Oliveira, F.S., dos, Santos, H.C., Cordeiro, P.W., and Almeida, S.Q., "Multivariate Calibration in Fourier Transform Infrared Spectrometry as a Tool to Detect Adulterations in Brazilian Gasoline", Fuel, Volume 87, No. 3, pp. 346-52, 2008.

[7] Lee, J., Chang, H.T., An, H., Ahn, S., Shim, J., and Kim, J-M., "A Protective Layer Approach to Solvatochromic Sensors", Nature Communications, Volume 4, pp. 2461-2469, 2013.

[8] Wu, J., Lu, X., Shan, F., Guan, J., and Lu, Q., "Polydiacetylene-Embedded Supramolecular Electrospun Fibres for a Colourimetric Sensor of Organic Amine Vapour", RSC Advances, Volume 3, No. 45, pp. 22841-22844, 2013.

[9] Yarimaga, O., Jaworski, J., Yoon, B., and Kim, J-M., "Polydiacetylenes: Supramolecular Smart Materials with a Structural Hierarchy for Sensing, Imaging and Display Applications", Chemical Communications, Volume 48, No. 19, pp. 2469-2485, 2012.

[10] Bhardwaj, N., and Kundu, S.C., "Electrospinning: A Fascinating Fiber Fabrication Technique", Biotechnology Advances, Volume 28, No. 3, pp. 325-347, 2010.

[11] Celebioglu, A., and Uyar, T., "Electrospun Gamma-Cyclodextrin ([gamma]-CD) Nanofibers for the Entrapment of Volatile Organic Compounds", RSC Advances, Volume 3, No. 45, pp. 22891-22895, 2013.

[12] Chae, S.K., Park, H., Yoon, J., Lee, C.H., Ahn, D.J., and Kim, J.M., "Polydiacetylene Supramolecules in Electrospun Microfibers: Fabrication, Micropatterning, and Sensor Applications", Advanced Materials, Volume 19, No. 4, pp. 521-524, 2007.

[13] Yoon, J., Jung, Y.S., and Kim, J.M., "A Combinatorial Approach for Colorimetric Differentiation of Organic Solvents Based on Conjugated Polymer Embedded Electrospun Fibers", Advanced Functional Materials, Volume 19, No. 2, pp. 209-214, 2009.

[14] Li, Y., Wang, L., Yin, X., Ding, B., Sun, G., Ke, T., Chen, J., and Yu, J., "Colorimetric Strips for Visual Lead Ion Recognition Utilizing Polydiacetylenes Embedded Nanofibers", Journal of Materials Chemistry-A, Volume 2, pp. 18304-18312, 2014.

[15] Bragança, FC., and Rosa, D.S., "Thermal, Mechanical and Morphological Analysis of Poly (å-Caprolactone), Cellulose Acetate and their Blends", Polymers for Advanced Technologies, Volume 14, No. 10, pp. 669-675, 2003.

[16] Han, J., Branford-White, C.J., and Zhu, L-M., "Preparation of Poly (å-Caprolactone)/ Poly(Trimethylene Carbonate) Blend Nanofibers by Electrospinning", Carbohydrate Polymers, Volume 79, No. 1, pp. 214-218, 2010.

[17] Xu, Y., Wang, C., Stark, N.M., Cai, Z., and Chu, F., "Miscibility and Thermal Behavior of Poly ([-Caprolactone)/Long-Chain Ester of Cellulose Blends", Carbohydrate Polymers, Volume 88, No. 2, pp. 422-427, 2012.

[18] Lee, J., Pyo, M., Lee, S-H., Kim, J., Ra, M., Kim, W-Y., Park, B.J., Lee, C.W., Kim, and J.M., "Hydrochromic Conjugated Polymers for Human Sweat Pore Mapping", Nature Communications, Volume 5, pp. 3736-3746, 2014.