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Colorimetric Sensor for Detection of Adulteration in Gasoline using Polydiacetylene Electrospun Fibers

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Abstract

We report the successful incorporation of pentacosadiynoic acid (PCDA) in poly(Ɛ-caprolactone) (PCL) by electro-spinning technique for sensor application. The UV-polymerization of the resulting electrospun fibers mats (EFMs) produced polydiacetylenes (PDA) polymer exhibiting blue color. The PCL-PDA EFMs were characterized by Raman Spectroscopy, UV-Vis spectroscopy and FE-SEM analysis. Sensor test results revealed that the treatment of the PCL-PDA EFMs with adulterated gasoline showed a blue to red color transition rapidly. FE-SEM images demonstrated that the thinner or toluene used as an adulterant in the gasoline destroyed the PCL electrospun fibers which gave access to PDA polymer producing red color.

Keywords: Poly(Ɛ-caprolactone); Electro-spinning; Adulterated gasoline; Thinner; Toluene.

Introduction

Gasoline is a complex mixture of chemical compounds that powers internal combustion engines throughout the world [1].The chemical composition of gasoline is not uniform across the world due to the different government laws and weather conditions [2]. In order to ensure safety of a vehicle, gasoline should meet certain standards established within a country. However, there are increasing number of incidents reported of adulterated or polluted gasoline [2]. Besides the obvious fiscal frauds, the addition of gasoline adulterants results in a reduction of engine lifetime and more generally in an increased environmental impact [3]. The detection of gasoline adulterants is a challenging jobin which lots of experiments are performed to ascertain the existence of various chemical compounds in the pure and spurious gasoline [4].

Polydiacetylenes (PDA) have an alternating ene-yne backbone structure [5-7].10,12-pentacosadiyonic acid (PCDA)($CH_3(CH_2)_{11}C{\equiv}C$-$C{\equiv}C(CH_2)_8COOH$), a frequently used DA monomer in PDA chemistry, was employed in our study. If PDAs are prepared under optimal conditions, they normally display a blue color with a λ_{max} = ~640 nm [8]. Interestingly, PDAs undergo a distinct color change (blue-to-red) when their arrayed p-orbitals are destroyed by environmental stimulations such as heating, mechanical pressing and exposure to organic solvents [9].

The electro-spinning technique allows for rapid and economical fabrication of fibrous polymer membranes with large surface area [10, 11]. Before electro-spinning, PCDA monomers are randomly dispersed in the organic solvent. As the solvent evaporates during electrospun fiber formation, self-assembly of PCDA monomers takes place due to the greater attractive forces existed in between PCDA monomers in comparison to the attractive forces present in between PCDA monomers and matrix polymer. The electrospun fibers are collected on the grounded metallic drum. Moreover, UV polymerization of the electrospun fiber mat (EFM) results in the formation of PDA polymer within matrix polymer [13, 14]. In the recent past, various

reports have been published in which PDA polymer was successfully embedded via electro-spinning technique [2, 12-14].

In this work, a sensor was fabricated by incorporating PDA polymer in poly(ε-caprolactone) (PCL) for a fast detection of the adulterated gasoline. PCL is an aliphatic polyester having reasonable physical properties for our sensor application, It is also a biodegradable polymer [15-17]; and thereby selected as a novel polymer matrix. No study was previously done in which the use of PCL is reported as a litmus-type sensor for detecting the adulterated gasoline in a short period of time.

Materials and Methods

10,12-Pentacosadiynoic acid (PCDA) and PCL were received from Sigma-Aldrich, Co., USA. The commercial grade toluene and thinner was used and the gasoline samples were purchased from a commercial petrol pump (PSO Pakistan) and used as-received.

Electro-spinning and photo-polymerization

Similar to our previous work reported earlier [18], the PDA-embedded polymer fibers were fabricated by the electro-spinning technique. Aviscous solution of PCL (9 wt.%) and PCDA (4 wt.%) was placedin a 10 ml plastic syringe; mounted on an automatic syringe pump. A high voltage (11 kV) is applied to a conductive capillary attached to the syringe needle causing ejection of a charged polymer jet from the polymer solution. The electrospun fibers were collected on the aluminum foil placed on the rotating collector.

UV-polymerization of the electrospun fibers mats (EFMs) was performed on a 254 nm UV light source (Spectro line ENF 260C/FE, USA).

Preparation of polymer film

We prepared polymer films for UV-Vis spectroscopy test. A viscous polymer solution of PCL (2 wt.%) and PCDA (2 wt.%) in chloroform was prepared and stirred overnight at room temperature. The polymer solution was spin-coated (MIKASA Opticoat Spin Coater MS-A-150, Japan) at 500 rpm on a glass slide for 20 s to fabricate the PCDA embedded PCL polymer film. Photo-polymerization of each polymer film was carried out under UV light (254 nm) for 180 s before the test.

Sensor test

The UV irradiated PCL-PDA EFMs were incubated in10 mL gasoline sample for 5-120s. A digital camera (Canon Power shot G12) was used to record the color transition (blue to red) of the EFM. In order to ensure reproducibility, each test was carried out multiple times.

Characterization

The formation of PDA polymer in PCL-PDA EFM was confirmed by Raman microscope, equipped with a diode laser (785 nm), a thermoelectrically cooled (-40^{o}C) charge-coupled detection (CCD) detector and a holographic grating (Kaiser Optical Inc., USA). Ultraviolet-visible (UV-Vis) absorption spectra of the spin-coated film were obtained using a UV-Vis spectrophotometer (S-4100 PDA, Scinco Co. Ltd, Korea). The surface morphology of EFMs was examined under FE-SEM (JSM 6701F, JEOL Japan).

Results and Discussion

Chemical structure of electrospun fibers

The Raman spectra of the PCDA solution and the UV irradiated PCL-PDA EFM are demonstrated in Fig. 1a and b. The peak located at 2255 cm^{-1} represents the acetylenic stretch Fig. 1a [2]. On the other hand, Fig. 1b displayed the appearance of two peaks located at 1450 cm^{-1} (C=C) and 2080 cm^{-1} (C≡C) corresponding to the conjugated alkene-alkyne groups formation [19] within the EFM; and the disappearance of the peak at 2255 cm^{-1}. These results revealed the formation of PDA polymer after UV irradiation, and are in close proximity with a previous report [2].

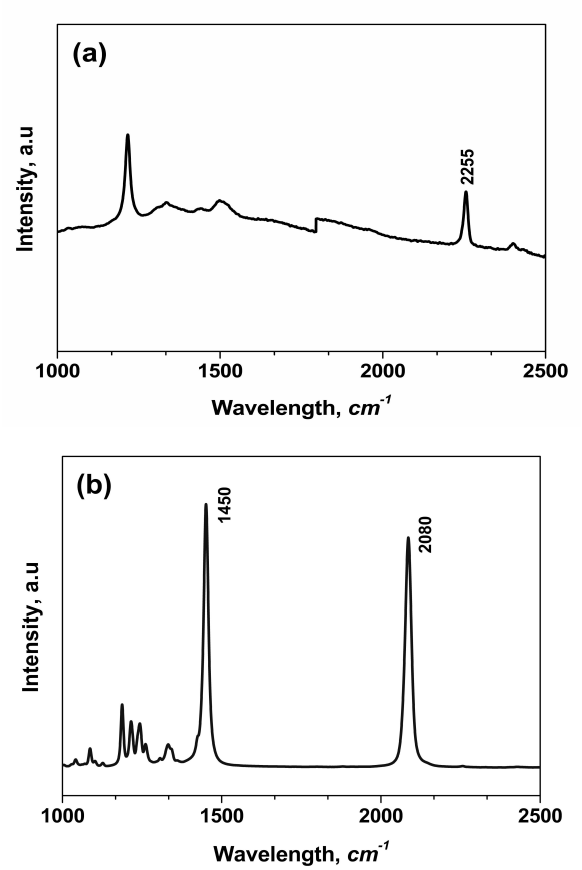

Figure 1. **Raman spectra of (a) PCDA solution (b) UV irradiated PCL-PDA EFM**

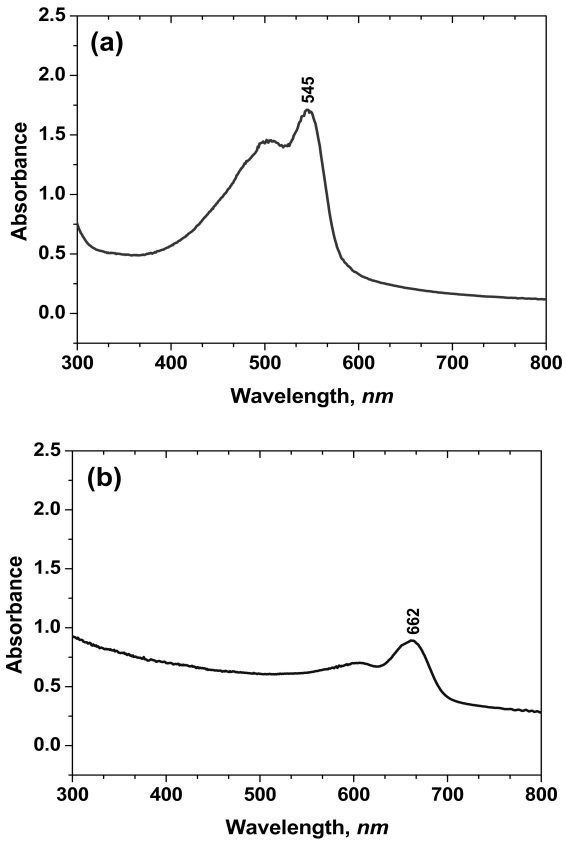

Figure 2. **UV-Vis spectra of (a) PCDA embedded PCL spin coated film (b) UV irradiated PCL-PDA spin coated film**

Fig. 2 shows the UV-Vis absorption spectra of PCL-PDA spin-coated film under UV light irradiation at 254 nm. It is evident from the Fig. 2 that a significant shift in the maximum wavelength from 545 nm to 662 nm takes place. This shift produces red-to-blue color change when the PCL-PDA spin-coated film was UV irradiated at 254 nm [20]. The findings revealed the formation of PDA polymer within the spin-coated film; and are in agreement with Raman spectra given in Fig. 1a and b.

Surface morphology of electrospun fibers

Fig. 3 demonstrates the FE-SEM images of EFMs. The images revealed the beadless morphology of the electrospun fibers as well as the dimensions of the each fiber remained un-changed after the 254 nm UV irradiation [6, 13].

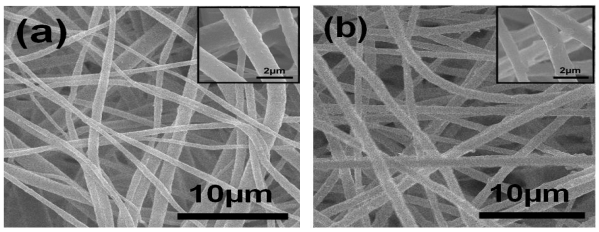

Figure 3. **FE-SEM images of PCL-PDA EFM (a) without UV light irradiation (b) UV light irradiated for 180 s**

Sensor test of commercial gasoline

After preliminary trials (results are not presented here), we have chosen PCL-PDA EFM (UV irradiation time - 180 s) for more investigations.

Fig. 4 displays the effect of commercial gasoline treatment of the PCL-PDA EFM for 120 s. It is evident that there was no blue-to-red color transition observed for PCL-PDA EFM (UV irradiation time - 180 s) Fig. 4. It could be due to

the presence of the fully polymerized PDA polymer within the EFM.

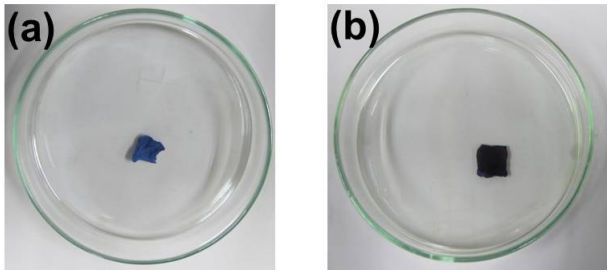

Figure 4. **Photographs of PCL-PDA EFMs irradiated with 254 nm UV light(a) without incubation in commercial gasoline (b) after incubation in commercial gasoline (UV irradiation time-180s, Incubation time-120s)**

Fig. 5 shows the smooth morphology of the electrospun fibers immersed in commercial gasoline for 120 s. It demonstrates that the physical structure of the PCL-PDA EFM remained intact after incubation in commercial gasoline.

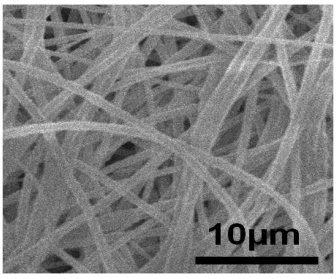

Figure 5. **FE-SEM image of PCL-PDA EFM after incubation in commercial gasoline (UV irradiation time-180 s, Incubation time-120s)**

Sensor test of gasoline adulteration

We further investigated the possibility of using PCL-PDA EFM as a potential sensor to detect adulterated gasoline. For preparing spurious gasoline; a 40% of thinner/toluene was added to pure gasoline (60%) and the results were demonstrated in Fig. 6a and b.

It is clear from the photographic images shown in Fig. 6a and b that PCL-PDA EFM treated with 40% thinner and 40% toluene caused chromatic transition from blue to red color of the mat after a short period of time (5 s). Interestingly, bright red color appeared for PCL-PDA EFM treated with 40% thinner in comparison to PCL-PDA EFM treated with 40% toluene.

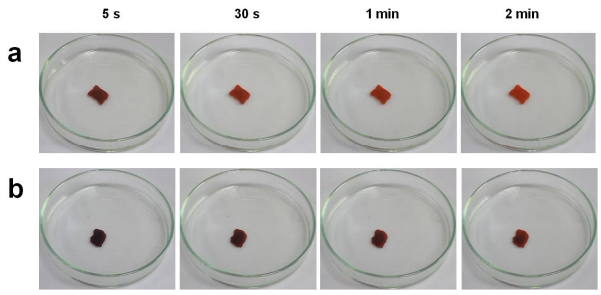

Figure 6. **Photographs of UV irradiated PCL-PDA EFMs after exposure to polluted gasoline *(a)* 40% Thinner*(b)* 40% Toluene (UV irradiation time-180 s)**

Furthermore, FE-SEM results of the mats revealed partially damaged fibrous structure after adulterated gasoline treatment Fig. 7. It allows diffusion of the spurious gasoline to the embedded PDA, causing chromatic transition (blue to red) of PDA polymer.

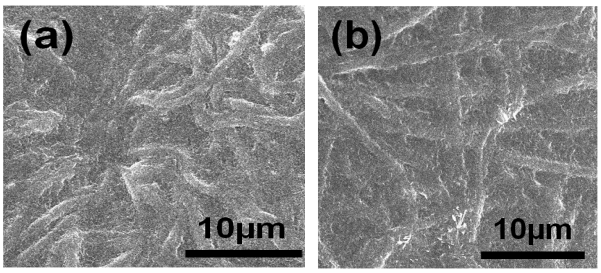

Figure 7. **FE-SEM images of PCL-PDA EFMs immersed in polluted gasoline *(a)*40% thinner *(b)* 40% toluene (UV irradiation time-180 s, Incubation time-120s**

Also, we have treated the PCL-PDA EFMs with the thinner and toluene to ascertain the reasoning behind the blue-to-red color transition of the mat. Fig. 8 shows the photographic images of the PCL-PDA EFM incubated in thinner and toluene for different time period. It can be seen from the Fig. 8 that the treatment with thinner Fig. 8a and toluene Fig. 8b caused color transition of the PCL-PDA EFM after short period of time (5 s).

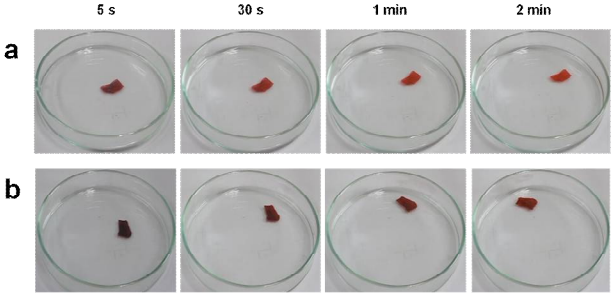

Figure 8. **Photographs of PCL-PDA EFMs incubated in the solvent *(a)* Thinner *(b)* Toluene (UV irradiation time-180 s)**

Moreover, FE-SEM analysis was carried out to determine the mechanism involved in the blue-to-red color transition of the mats when incubated in thinner and toluene. As displayed in Fig. 9, treatment of the mats with thinner and toluene was resulted into the breakdown of the fibrous structure producing color transition. Hence, it was revealed that thinner and toluene are responsible for the dissolution of PCL electrospun fibers resulting in the chromatic transition of the mats.

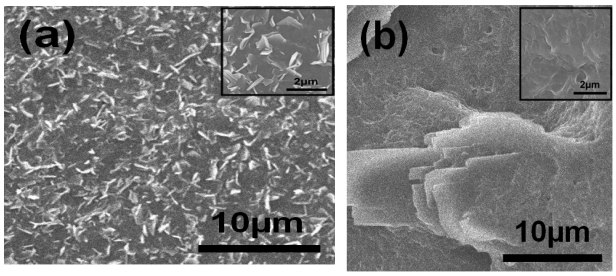

Figure 9. **FE-SEM images of PCL-PDA EFMs incubated in the solvent (a) Thinner (b) Toluene (UV irradiation time-180 s, Incubation time-120s**

Conclusion

We have successfully prepared a novel litmus-type sensor based on PCL-PDA EFM for detecting the adulterated gasoline within 5s. We found that UV irradiation time should be 180 s for producing PDA polymer within EFM. We revealed that chromic transition (blue to red) of the EFM was quickly achieved as our proposed sensor exposed to adulterated gasoline. We also found that the thinner and the toluene used as an adulterant; dissolved the PCL electrospun fibers and allows penetration of the spurious gasoline to the embedded PDA.

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References

1. L. Wiedemann, L. d'Avila and D. Azevedo, *Fuel.,* 84 (2005) 467.
2. J. Lee, S. Balakrishnan, J. Cho, S.-H. Jeon and J.-M. Kim, *J. Mater. Chem.,* 21 (2011) 2648.
3. N. Wiziack, A. Catini, M. Santonico, A. D'amico, R. Paolesse, L. Paterno,F. Fonseca and C. Natale, *Sens. Actuators, B.,* 140 (2009) 508.
4. L. S. Teixeira, F. S. Oliveira, H. C. dos Santos, P. W. Cordeiro and S. Q. Almeida, *Fuel.,* 87 (2008) 346.
5. J. Lee, H. T. Cszhang, H. An, S. Ahn, J. Shim and J.-M. Kim, *Nat. Commun.,* 4 (2013) 2461.
6. J. Wu, X. Lu, F. Shan, J. Guan and Q. Lu, *RSC. Adv.,* 3 (2013) 22841.
7. B. Yoon, J. Lee, I. S. Park, S. Jeon, J. Lee, and J.-M. Kim, *J. Mater. Chem. C.,* 1 (2013) 2388.
8. X. Chen and J. Yoon, *Dyes Pigm.,* 89 (2011) 194.
9. O. Yarimaga, J. Jaworski, B. Yoon and J.-M. Kim, *Chem. Commun.,* 48 (2012) 2469.
10. N. Bhardwaj and S. C. Kundu, *Biotechnol.Adv.,* 28 (2010) 325.
11. A. Rogina, *Appl. Surf. Sci.,* 296 (2014) 221.
12. S. K. Chae, H. Park, J. Yoon, C. H. Lee, D. J. Ahn and J. M. Kim, *Adv. Mater.,* 19 (2007) 521.
13. J. Yoon, Y. S. Jung and J. M. Kim, *Adv. Funct. Mater.,*19 (2009) 209.
14. Y. Li, L. Wang, X. Yin, B. Ding, G. Sun, T. Ke, J. Chen and J. Yu, *J. Mater. Chem. A,* 2 (2014) 18304.
15. F. C. Bragança and D. S. Rosa, *Polym. Advan. Technol.,* 14 (2003) 669.
16. J. Han, C. J. Branford-White and L.-M. Zhu, *Carbohyd. Polym.,* 79 (2010) 214.
17. Y. Xu, C. Wang, N. M. Stark, Z. Cai and F. Chu, *Carbohyd. Polym.,* 88 (2012) 422.
18. A. Khatri, S. Ali, A. K. Jhatial and S. H. Kim, *Color. Technol.,* 131 (2015) 374.
19. A. Wu, Y. Gu, C. Stavrou, H. Kazerani, J. F. Federici and Z. Iqbal, *Sens. Actuators, B.,* 203 (2014) 320.
20. R. Jelinek and M. Ritenberg, *RSC. Adv.,* 3 (2013) 21192.