

Polyaniline-TiO₂ Hybrid-Coated Cotton Fabric for Durable Electrical Conductivity

K. U. Savitha, H. Gurumallesh Prabu

Department of Industrial Chemistry, School of Chemistry, Alagappa University, Karaikudi, India

Correspondence to: H. G. Prabu (E-mail: hgprabu2010@gmail.com)

ABSTRACT: A polyaniline-TiO₂ hybrid was coated on cotton fabric to make it electrically conductive. A One-pot method of synthesis with acetic acid medium was used, in which TiCl₄ was used as precursor. The oxidative polymerization of aniline adsorbed on TiO₂ (anatase form) was performed in the presence of cotton fabric. Fabric crystallinity was least affected by the coatings, as confirmed by XRD analysis. FTIR studies revealed interactions between fiber and hybrid. The morphological study through SEM showed the uniform coating of hybrid over the fibers of the cotton fabric and AFM analysis revealed the rod-like structure of the hybrid. The strength of the coated fabrics was assessed using abrasion tests. The electrical conductivity was determined using electrochemical impedance spectroscopy (EIS). The conductivity value varied with respect to TiO₂ content and ranged in the order 10⁻⁴ to 10² S/cm. The effect of atmospheric aging was assessed. A more durable conductivity was observed in hybrid-coated fabric than pristine polyaniline-coated fabric. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000-000, 2012

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INTRODUCTION

Polyaniline-TiO₂ composites/hybrids are highly tunable materials with unique electrical and optical properties.^{1,2} The electrical conductivity, electro-magnetic interference (EMI) shielding, electrochromic stability, and optical contrast of polyaniline are enhanced by the addition of TiO₂. The electrical conductivity of the composites are reported to increase initially with TiO₂ content and then decrease on excess of TiO₂. This initial increase is attributed to the well-extended conjugation conformation of doped polyaniline and decrease on excess concentration of TiO₂, which attributes to the particle blockade of conducting path.³ The high-electrochromic stability and optical contrast are by the virtue of electron-donor acceptor interactions between polyaniline and TiO₂.⁴ The EMI shielding capacity is the contribution of enhanced dielectric constant of the composite.⁵

The main problem encountered by the composite/hybrid is processibility. Coating of these composite/hybrids onto textiles serves dual purpose: (i) it solves the problem of processibility by extending the mechanical strength and flexibility contributed by textile component and (ii) it serves as functional conductive textiles, where demand for conducting textile materials is

increasing day-by-day. Electrically conductive textiles find vast applications as wearable electronics,⁶ de-electrifying coatings, EMI shield materials,⁷ ESD materials, and special purpose clothings that are dust and germ-free.⁸ The polyaniline-TiO₂ hybrid-coated fabric is expected to show photo-catalytic properties and photo-sensing properties.

There are many reports describing the conducting-polymer coatings on textiles. Polyaniline,⁹⁻¹⁵ polypyrrole,¹⁶⁻¹⁸ and PEDOT^{19,20} have been explored for such electrically conducting coatings on textile materials. Among these conducting polymers, polyaniline finds an important position due to its easiness of synthesis, electrical conductivity, and stability.²¹ Textile materials and paper have been coated with polyaniline in various methods as *in situ* polymerization,¹¹⁻¹³ electrochemical deposition,¹⁴ and template process.¹⁵ The major disadvantage in *in situ* polymerization of polyaniline is the adverse effect on the strength of fabric due to highly acidic pH. The electrochemical method is also difficult due to the insulating nature of the fabric. Very recently, polyaniline-ZnO coatings on fabrics for conductive network was studied and reported by Zhao et al.²² To the best of our knowledge, polyaniline-TiO₂ coatings are not performed on fabrics. Hence, it is aimed in this study to explore the

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Table I. The %Weight Gain and % TiO₂ Content in the Hybrid-Coated Textiles

| Coated fabric | %Weight gain | % TiO ₂ |
|---------------|--------------|--------------------|
| C0.1 | 21.1 | 2.11 |
| C0.2 | 22.5 | 4.5 |
| C0.3 | 25.3 | 7.59 |
| C0.4 | 23.2 | 9.2 |
| C1 | 12.7 | 6.2 |

possibilities of coating of polyaniline–TiO₂ on cotton to impart unique properties of the hybrid into flexible form. The coated fabric is expected to possess UV-protective²³ and self-cleaning property²⁴ of TiO₂ with minimum adverse effect on strength.

EXPERIMENTAL

Titanium tetrachloride (Loba), acetic acid (E. Merck), ammonium persulfate (Fisher), and camphor sulfonic acid (Sigma-Aldrich) were used as such without any further purification. Aniline (CDH) was distilled before use. Woven-cotton fabric of 80 s count was obtained from SITRA, Coimbatore. It was desized and scoured following conventional procedures. Two milliliters of titanium tetrachloride (TiCl₄) was digested in 10 mL of alcohol with constant stirring. A 0.6-mL of aniline was added synchronously with 1.3 mL of alcoholic TiCl₄ solution into a flask containing 40 mL of acetic acid (1 M). The temperature was increased to 80°C and stirring was continued for 4 h. Aniline-adsorbed TiO₂ colloidal solution was thus prepared and cooled at room temperature. Accurately weighed cotton fabric was hanged without crease using two concentric rings, just to immerse in the colloidal solution containing the synthesized TiO₂ with aniline adsorbed on it. Fabric was fully impregnated with the solution by continuous stirring for 1 h. Then required amounts of ammonium persulfate (APS) at 1:1 molar ratio with aniline and camphor sulfonic acid (CSA) at 1:0.5 molar ratio with aniline were added as aqueous solutions and polymerization was continued for 2 h at room temperature. Then this coated fabric was washed well with distilled water and dried. Thus cotton fabric with 1:0.3 ratio of polyaniline–TiO₂ was obtained and designated as C_{0.3}. Likewise, coated fabrics of C_{0.1}, C_{0.2}, C_{0.4}, and C₁ were prepared by coating corresponding hybrids following aforementioned procedure for understanding the influence of TiO₂ in electrical conductivity. For comparison purpose, pristine polyaniline coated cotton was produced by *in situ* chemical polymerization technique in HCl as detailed elsewhere^{11–13} and referred as C₀.

Characterization

XRD analysis was performed for coated fabric using XPERT PANALYTIC instrument. All samples were analyzed in the range between 10 and 80° as 2θ and Cu as anode (K-Alpha-1.54060 Å). Coated-fabric sample was crushed and pelleted using KBr and subjected to FTIR analysis on SHIMADZU 8400S FTIR spectrophotometer. The surface morphology of sample was examined by Nikon-H-550L optical microscope, HITACHI S3000H scanning electron microscope, and Veeco-II Atomic force microscope. Thermal analysis was performed using an

EXSTAR Model 6000 instrument with a heating rate 20°C/min over a temperature range between 40 and 750°C in air. The electrochemical impedance spectroscopy (EIS) experiments were performed by sandwiching fabric sample between two symmetrical stainless steel electrodes in AUTOLAB electrochemical impedance bridge with FRA software. The frequency scan was performed from 10 mHz to 1 MHz with 0.1 V amplitude. The *I*–*V* (current–voltage) curve was recorded using CH 620A instrument. Abrasion test was carried out in a crock meter.

RESULTS AND DISCUSSION

PANI–TiO₂ hybrid coating on cotton produced electrically conducting fabric and conductivity was comparable with pristine PANI-coated fabric. A weight gain of 20% was observed with pristine PANI-coated fabric, while the weight gain varied with respect to the ratio of TiO₂ in the case of hybrid-coated fabrics (Table I). When the TiO₂ content was increased, the weight gain increased up to a ratio of 1:0.3 and then decreased. This decrease may be due to the lower adhesion of hybrids with high TiO₂ content.

XRD

The XRD pattern (Figure 1) of polyaniline–TiO₂-coated cotton fabric was almost similar to that of uncoated-cotton fabric. Both belong to cellulose-A structure as reported in the published reports.²⁵ The XRD peaks of uncoated cotton were at 2θ values of 14.9 and 22.7 corresponding to 101 and 002 plane, respectively. These peaks were slightly shifted to higher values of 2θ at 15.3 and 22.9 for coated fabric with a small shift in interplanar (*d*) spacing. This shows the diffusion of hybrid into amorphous and para-crystalline regions of cotton fabric, without affecting its crystallinity. The result is similar to that reported by Bhat et al. for polyaniline coated cotton fabric.¹² The XRD analysis of hybrid in powder form confirmed the formation of polyaniline–TiO₂ (Figure 1, insight). The hybrid formed showed the characteristics of both polyaniline and TiO₂. The badly crystallized peaks around 2θ of 15–20 correspond to polyaniline. The peak at 2θ of 25.35 representing 101 plane

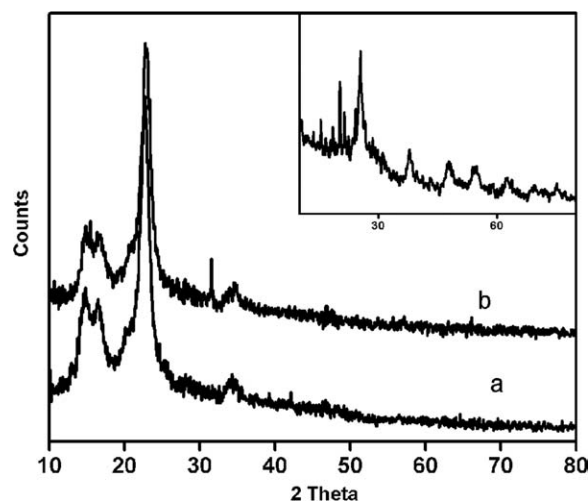


Figure 1. XRD patterns of (a) uncoated cotton, (b) coated cotton, insight polyaniline–TiO₂ hybrid.

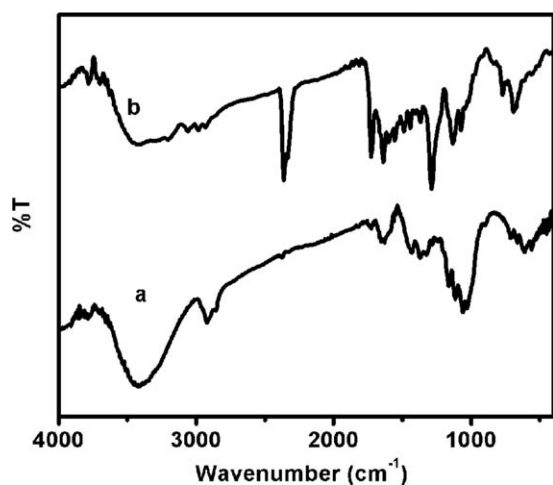


Figure 2. FTIR spectra of (a) uncoated cotton, (b) coated cotton.

confirms that TiO_2 is of anatase phase (JCPDS file no 89-4203, tetragonal primitive). The formation of polyaniline– TiO_2 in acetic acid medium has resulted anatase phase, while rutile phase was reported in HCl medium.^{26,27}

FTIR

The FTIR spectra of hybrid-coated fabric and uncoated fabric are given in Figure 2. Characteristic bands for polyaniline were present (around 3465, 1720, 1581, and 1290 cm^{-1}) in hybrid-coated fabrics. A shift in frequency was observed toward higher energy due to the interaction between fabric and hybrid material. The peak at 2906 cm^{-1} observed for uncoated fabric was due to the CH_2 anti-symmetric stretching vibrations of secondary CH_2OH groups in the glucose units of cellulose. This peak was absent in the spectra of the hybrid-coated fabric because of the interaction of hybrid with CH_2OH groups in the glucose units of cellulose. Hence, it is deduced that polyaniline part of the hybrid was attached to cellulose by hydrogen bridges. Major interaction of cotton fabric is with polymer part (polyaniline) of the hybrid. A strong band around 2360 cm^{-1} present in the coated fabric indicated charge–transfer interactions between hybrid and fabric through the Lewis acid site $-\text{Ti}^{4+}$. The peak corresponding to CSA was not found in the spectra.

Morphological Studies

The optical microscopic studies at 40 \times magnification clearly showed the encapsulation of cotton fibers by the hybrid (Figure 3). The SEM image confirms this observation. The intersites of

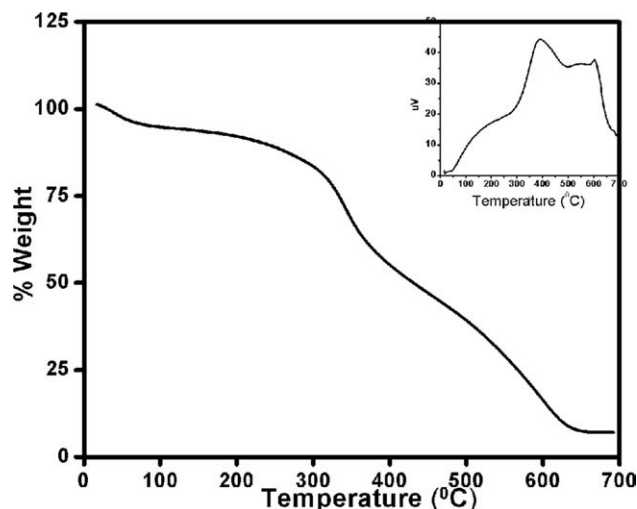


Figure 4. TGA spectra of $\text{C}_{0.3}$. Inset DTG spectra.

the fabric were not deposited with the hybrid. The coating was uniform at microscopic level but corrugated at further magnification. The morphology and topography of hybrid on the fiber was also observed through AFM technique. The AFM 3D image (2 mm \times 2 mm) of coating is given in Figure 3(d) and it showed an average roughness of 7.00 nm. A further magnified image (2D) 500 nm \times 200 nm showed that hybrid particle coating was grooved to form rod-like structures. The line profile (given in Supporting Information) indicated that the features detected by AFM [Figure 3(e)] had the average sizes in the plane (horizontal) and out of plane (vertical) directions as 2–24 nm and 3–8 nm, respectively.

Thermal Analysis

The thermogram of hybrid-coated cotton fabric ($\text{C}_{0.3}$) is shown in Figure 4. From the TGA curve, the weight loss due to moisture (at around 100 $^\circ\text{C}$), fiber degradation (at around 300 $^\circ\text{C}$), and polyaniline degradation (at around 500 $^\circ\text{C}$) can be clearly observed. The DTG curve shown in inset explains these findings more clearly. The absence of relevant weight loss around 200 $^\circ\text{C}$ indicated low content of CSA. CHNS/O analysis was performed for pristine PANI and PANI– TiO_2 hybrid powders using Elemental analyse'n'systeme instrument (GmbH varioMicroV1.6.1), to estimate the approximate CSA content. It was observed that the % sulfur content of pristine PANI and PANI– TiO_2 hybrid were 18.0 and 6.8, respectively. Hence, it can be deduced that the doping with CSA is somewhat prevented by

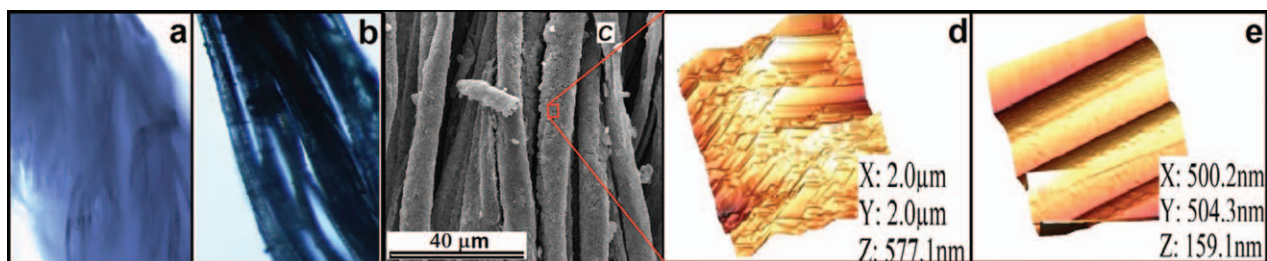


Figure 3. (a) Optical microscopic image of uncoated cotton, (b) optical microscopic image of coated cotton, (c) SEM image of coated cotton, (d, e) AFM images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

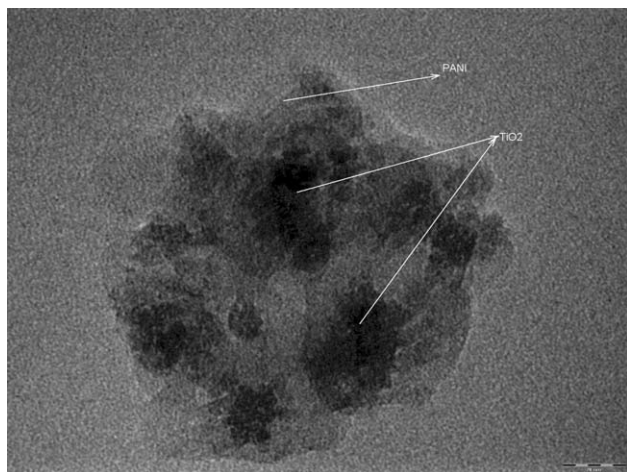


Figure 5. TEM image of PANI–TiO₂ hybrid.

the presence of TiO₂. The amount of hybrid present on the fabric calculated from TGA curve was about 25% and that of TiO₂ content was about 6%. This shows that TiO₂ content in hybrid was same as in feed ratio.

Electrical Conductivity Studies

The result of EIS shows that the TiO₂ content plays a major role in the electrical conductivity of the coated fabric. The real impedance decreased with frequency for all samples. The conductivity obtained was in the range from 10³ to 10⁵ Ω cm (Nyquist and bode plot are shown in Supporting Information). This range of conductivity is similar to the reported conductivity (10–275 kΩ) for PET fabric coated with polyaniline–ZnO composite.²² The conductivity of hybrid-coated fabrics was in the order C_{0.1} < C_{0.2} < C_{0.3} > C_{0.4} > C₁. This initial increase in conductivity up to C_{0.3} and subsequent decrease is in agreement with the previous reports, which confer the credit to the well-extended conjugation conformation of polyaniline and blocking due of TiO₂.³ The electrical conductivity can be enhanced by developing better orientated defect-free conducting polymers.²⁸ As detailed in the published reports,²⁹ TiO₂ may act as suitable template for the formation of well-oriented polyaniline. The TEM image of powder hybrid (corresponded to C_{0.3}) is given in Figure 5. It showed the TiO₂ core with polyaniline shell, which substantiated that PANI is formed over the TiO₂ surface. This might have influenced for the increase in conductivity observed up to C_{0.3}. When the TiO₂ content was further increased, the amount of hybrid coated onto fabric decreased (Table I). This lower the electrical conductivity of hybrid-coated fabrics with higher TiO₂ content. Additionally, increased amount of TiO₂, it may hinder the carrier transport between different molecular chains of polyaniline.

The electrical conductivity of coated fabric was also measured using potential–current (*I*–*V*) analysis (shown in Supporting Information). For the hybrid-coated fabric of C_{0.3}, the conductivity was found to be 1.5 × 10^{−3} S/cm, which is in good agreement with EIS result. Pristine polyaniline-coated fabric (C₀) was more conductive (2.2 × 10^{−3} S/cm) than all hybrid-coated fabrics studied. During treatment of TiCl₄ with alcohol four moles of HCl will be released and may be used up by aniline-forming

aniline hydrochloride, which in turn, is polymerized into polyaniline. Thus, CSA incorporation will be reduced with HCl content and may be the reason for the low conductivity of hybrid on comparing with pristine PANI. Moreover, the electrons from polyaniline is donated to TiO₂ forming a bonded interaction, which may also cause decrease in carrier availability.

Aging Study

The electrical conductivity of coated fabrics was monitored over a period of 1 week. The conductivity loss in the case of hybrid-coated fabrics was very low, while pristine polyaniline-coated cotton lost 50% of conductivity within the observed time period (Figure 6). This loss may be due to the degradation mechanisms as discussed by Travers's research group.^{30,31} Three main mechanisms described by them were dedoping, oxidation, and chemical crosslinking. The ordered-configuration of the hybrid can decrease the O₂ diffusion and thereby, reduce the loss by oxidation. As the initial amount of dopant is low, the effect of dedoping may be less significant. Thus, in this case of hybrid-coated fabrics, the occurrence of degradation mechanisms may be low.

Abrasion Test

The level of adhesion of hybrid material coated on cotton was experimented with surface abrasion tests and subsequent measurement of weight of fabric before and after coating (given in Supporting Information). The weight loss of the hybrid-coated fabrics was found to be negligible even after 50 abrasions with maximum loss of 2% for C₁. The weight loss may be due to the removal of loosely attached hybrid materials. The weight loss increased with decrease in polyaniline content. This suggests that the polymer part (polyaniline) act as a binding material. The presence of binding interactions between polyaniline and OH groups of cotton confirmed by FTIR analysis supports this inference. Pristine polyaniline-coated fabric could not withstand well even for 20 abrasions and resulted to tear-off. This shows that pristine polyaniline-coated fabric turns mechanically weak because of higher damage with HCl medium in the polymerization bath. The hybrid-coated fabric maintained its strength due

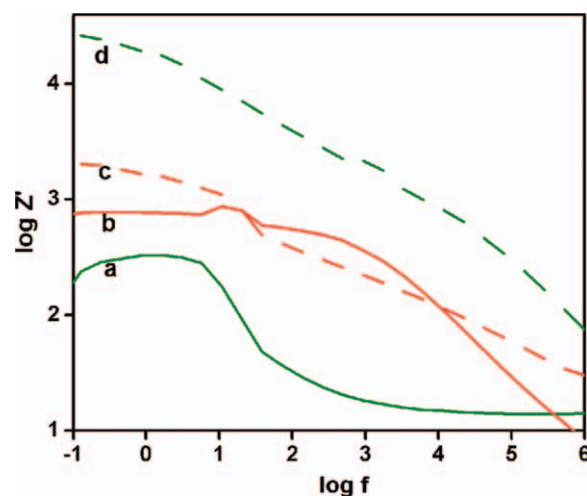


Figure 6. Bode plots of (a) C₀ before aging, (b) C_{0.3} before aging, (c) C_{0.3} after aging, (d) C₀ after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to negligible damage with acetic acid medium in the polymerization bath.

Advantageous of Hybrid-Coated Fabric

Two major challenges retarded the wide acceptance of pristine polyaniline coated fabric were (i) loss of electrical conductivity on aging and (ii) loss of strength of fabric (especially with cotton in highly acidic polymerization bath). These problems could be solved with the use of hybrid (polyaniline–TiO₂)-coated cotton fabric, in which the electrical conductivity loss was minimum and fabric strength was maintained. Since byproduct or wastage was less during the hybrid coating, this one-pot method can be termed as greener route. In the published reports on PANI–ZnO-coated PET fabric, ZnO interacts with PET fabric. In our study, there was no direct interaction between TiO₂ and cotton fabric as evidenced by FTIR data. Hence, the strength loss of cotton due to TiO₂ is negligible.

CONCLUSION

Cotton fabric was made electrically conductive with coating of polyaniline–TiO₂ hybrid. The coatings had negligible effect on crystallinity of the fabric. The electrical conductivity loss during aging was very less in the hybrid-coated fabric than the pristine polyaniline-coated fabric. By this one-pot method, cotton fabric of good adhesion, durable electrical conductivity, and good mechanical strength were produced.

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REFERENCES

1. Ram, M. K.; Yavuz, O.; Lahsangah, V.; Aldissi, M. *Sens. Actuators B* **2005**, *106*, 750.
2. Wu, C. G.; DeGroot, C.; Marcy, H. O.; Schindler, J. L.; Kannewurf, C. R.; Liu, Y. J. *Chem. Mater.* **1996**, *8*, 1992e.
3. Li, X.; Chen, W.; Bian, C.; He, J.; Xu, N.; Xue, G. *Appl. Surf. Sci.* **2003**, *217*, 16.
4. Xiong, S. X.; Wang, Q.; Xia, H. S. *Synth. Met.* **2004**, *146*, 37.
5. Mo, T.; Wang, H. W.; Chen, S. Y.; Yeh, Y. C. *Ceram. Int.* **2008**, *34*, 1767.
6. Hu, L.; Pasta, M.; Mantia, F. L.; Cui, L. F.; Jeong, S.; Deshazer, H. D.; Choi, J. W.; Han, S. M.; Cui, Y. *Nano Lett.* **2010**, *10*, 708.
7. Dhawan, S. K.; Singh, N.; Venkatachalam, S. *Synth. Met.* **2002**, *129*, 261.
8. Oh, K. W.; Hong, K. H.; Kim, S. H. *J. Appl. Polym. Sci.* **1999**, *74*, 2094.
9. Neelakandan, R.; Madhusoothanan, M. J. *Eng. Fibers Fabrics* **2010**, *5*, 25.
10. Kim, B.; Toncer, V.; Devause, E.; Dufour, C.; Viallier, P. *Synth. Met.* **2004**, *146*, 167.
11. Nasybulin, E.; Menshikova, I.; Sergeev, V.; Levon, K. J. *Appl. Polym. Sci.* **2009**, *114*, 1643.
12. Bhat, N. V.; Seshadri, D. T.; Radhakrishnan, S. *Tex. Res. J.* **2004**, *74*, 155.
13. Johnston, J. H.; Moraes, J.; Borrmann, T. *Synth. Met.* **2005**, *153*, 65.
14. Bhadani, S. N.; Sen Gupta, S. K.; Sahu, G. C.; Kumari, M. J. *Appl. Polym. Sci.* **1996**, *61*, 207.
15. Wu, J.; Zhou, D.; Looney, M. G.; Waters, P. J.; Wallace, G. G.; Too, C. O. *Synth. Met.* **2009**, *159*, 1135.
16. Subianto, S.; Will, G. D.; Kokot, S. *Int. J. Polym. Sci.* **2005**, *54*, 141.
17. Wang, L.; Lin, T.; Wang, X.; Kaynak, A. *Fibers Polym.* **2005**, *6*, 259.
18. Lin, T.; Wang, L.; Wang, X.; Kaynak, A. *Thin Solid Films* **2005**, *479*, 77.
19. Knittel, D.; Schollmeyer, E. *Synth. Met.* **2009**, *159*, 1433.
20. Kim, H. H.; Kim, M. S.; Song, K.; Park, Y. H.; Kim, S. H.; Joo, J.; Lee, J. Y. *Synth. Met.* **2003**, *106*, 135.
21. Manisankar, P.; Vedhi, C.; Selvanathan, G.; Gurumalles Prabu, H. *Electrochim Acta* **2006**, *51*, 2964.
22. Zhao, Y. P.; Cai, Z. S.; Zhou, Z. Y.; Fu, X. L. *Thin Solid Films* **2011**, *519*, 5887.
23. Erdem, N.; Erdogan, U. H.; Cireli, A. A.; Onar, N. J. *Appl. Polym. Sci.* **2010**, *115*, 152.
24. Mihailovic, D.; Saponjic, Z.; Radoicic, M.; Radetic, T.; Jovancic, P.; Nedeljkovic, J.; Radetic, M. *Carbohydr. Polym.* **2010**, *79*, 526.
25. Zhao, H.; Kwak, J. H.; Conrad, Z.; Arey, W.; Holladay, J. E. *Carbohydr. Polym.* **2007**, *68*, 235.
26. Savitha, K. U.; Gurumalles Prabu, H. *Mater. Chem. Phys.* **2011**, *130*, 275.
27. Bitao, S.; Shixiong, M.; Shixiong, S.; Yongchun, T.; Jie, B. *Front. Chem. China* **2007**, *2*, 123.
28. Bowman, D.; Mattes, B. R. *Synth. Met.* **2005**, *154*, 29.
29. Kim, B. S.; Lee, K. T.; Huh, P. H.; Lee, D. H.; Jo, N. J.; Lee, J. O. *Synth. Met.* **2009**, *159*, 1369.
30. Rannou, P.; Nechtschein, M.; Travers, J. P.; Bernera, D.; Walter, A.; Djurado, D. *Synth. Met.* **1999**, *101*, 734.
31. Berner, D.; Rannou, P.; Travers, J.P.; Djurado, D. *J. Chem. Phys.* **1998**, *95*, 1414.