

The Enhanced Electrical Conductivity of Cotton Fabrics Via Polymeric Nanocomposites

Cem Güneşoğlu*, Sinem Güneşoğlu, Suying Wei¹, and Zhanhu Guo²

Textile Engineering Department, Gaziantep University, Gaziantep 27310, Turkey

¹*Department of Chemistry and Physics, Lamar University, Beaumont TX 77710, USA*

²*Department of Chemical and Biomolecular Engineering, University of Tennessee Knoxville, Knoxville TN 37996, USA*

(Received October 7, 2015; Revised February 13, 2016; Accepted February 22, 2016)

Abstract: Enhanced electrical conductivity of cotton fabrics coated with polyaniline (PANI) and PANI/carbon coated Fe (Fe@C) and carbon coated Co (Co@C) metal nanoparticles (NPs) composites were investigated. PANI/metal nanoparticle (NP) composites were fabricated with a surface initialized polymerization method and silanization helped with chemical bonding to cotton. The volume resistivity of the samples and structural characterizations were assessed by relevant methods. The results showed that enhanced electrical conductivity, thermal stability and magnetization were obtained via polymeric nanocomposites (PNC) and all these findings revealed that PANI/metal NP PNC coated cotton fabrics would exhibit good level electromagnetic shielding performance as a function of combined electrical conductivity and magnetization which is the objective of our future studies.

Keywords: Conductive polymer, Metal nanoparticle, Polymeric nanocomposite

Introduction

General approaches to enhance the selected properties of textile fabrics include the embedment of relevant non-textile particles within the structure or covering the surface with those particles via various techniques. Electrical conductivity of textile fabrics has gained great interest among researchers. This is due to fact that traditional fibers that are used in the textile fabrics are electrically insulating materials and adding some conductivity can bring new usage areas for textile fabrics, especially for health-related topics like antistatic and electromagnetic shielding [14]. The widely accepted technical approach for increasing conductivity of textile fabrics is the incorporation of stainless steel and copper wire as conductive fillers; however the existence of metal wires causes an increase in the fabric thickness which is accepted as variation source on surface resistance [5]. Therefore, coating conductive polymers (CP) onto textiles may lead power to flow through without the incorporation of any wiring throughout the fabric. There are some studies on coating textile fibrous surfaces with conductive polymers like polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) via electrochemical and chemical polymerization upon insulating fiber or preparation of composite conductive fibers by chemical or electrochemical routes [6-13]. Among these polymers, PANI has been defined to be the first dispersible inherently conductive polymer readily accessible and stable in ambient conditions. It has ability to switch very quickly between insulating and conductive forms when exposed to an acidic or alkaline environment. It also has low cost and relatively simple chemical and electrochemical polymerization

techniques [14-17].

Metallic based CP nanocomposites are explored in view of great variety of applications and improved electron transfer and eventually achieved synergistic effect due to the combination of the electrocatalytic performances of the composite constituents are expected. Therefore, one particular research objective has been the dispersion of metal nanoparticles (NPs) within the polymer matrix, since the incorporation of metal nanoparticles is known to enhance the conductivity of the polymer and add magnetization [18-20]. Additionally, metal nanoparticles embedded in CP matrix are claimed to serve as efficient electrocatalysts during oxidation and reduction of monomer. Other advantages of these nanoparticles are arranging CP into well-defined structure, avoiding aggregation and providing controllable particle size for nanocomposites [21-23]. As a result, the textile surfaces covered with CP/metal nanoparticle are expected to have a good level of electrical conductivity and some magnetization which are key factors for EMR shielding property.

This study has been conducted to investigate the enhancement of electrical conductivity of 100 % cotton knitted textile fabric after covering it with conductive polymer/metallic particle nanocomposites via completing the polymerization of CP in the presence of fabric. The characterizations of the samples with SEM, FTIR, TGA and PPMS were also included.

Experimental

Materials

100 % knitted cotton fabric (15×22 wale/course, 270 g/m²) was used in this study. The fabric was scoured and

*Corresponding author: gunesoglu@gantep.edu.tr

bleached by the supplier (Selçuk Tekstil, Gaziantep, Turkey). Aniline monomer (C_6H_7N), ammonium persulfate as the oxidant ($APS, (NH_4)_2S_2O_8$), p-toluene sulphonic acid as the protonic doping agent (PTSA, $C_7H_8O_3S$) were purchased from Sigma Aldrich. The metal nanoparticles were selected as carbon coated Fe ($Fe@C$) and carbon coated Co ($Co@C$) which are widely investigated magnetic encapsulates with average particle size of 20 nm. They were obtained from Nanjing Emperor Nano Material Co., Ltd. The metal nanoparticles were subjected to silanization with (3-aminopropyl)-triethoxysilane (APTES, $C_9H_{23}NO_3Si$ from Sigma Aldrich) before polymerization of aniline. All the chemicals were used as-received without any further treatment.

Preparation of PANI/NP PNCs

PANI/metal nanoparticle (NP) composites were fabricated with a surface initialized polymerization method [24]. First, the NPs (1 % of weight of fabric sample) were dispersed in toluene by 1-h sonication; then fabric sample was added within the dispersion and stirring was kept on for 30 minutes. APTES solution in toluene (~0.1 % M) was prepared by 1-h vigorous stirring. The fabric sample (with NPs on it) was added into APTES solution, followed by 1-h ultrasonic stirring; then the sample was refluxed at 120 °C for 30 minutes for silanization. Theoretically, alkoxy groups produced over C shell of NP after silanization would make Si-O bond with the hydroxyl groups of cotton. Then the sample was dropped in the aniline solution in distilled water with a liquor ratio of 1:50. The liquor ratio is simply the mass of aniline solution prepared per unit mass of sample being treated. The molar ratio of APS: Aniline: PTSA in that solution was 1:1.25:1 and molar volumes of aniline were varied for several applications; and the solution was sonicated for 2-h in an ice-water bath for polymerization. The solution was filtered and the sample was washed with ammonia several times to receive undoped PANI, and then further washed with distilled water. After doping PANI in the excess of 0.5 M HCl, filtering and washing with distilled water were employed again. The sample was finally dried overnight in laboratory environment. The repeated undoping/doping process was done to enhance conductivity due to proper doping level as reported elsewhere [25,26]. As a reference sample, pure PANI was also fabricated following the above procedures without adding any NPs for comparison.

Characterization

The morphology of nanocomposite over cotton fibre was evaluated via SEM (Hitachi 3400 N), size distribution and cluster formation were also assessed. FT-IR characterizations were carried out using a Bruker Inc. Tensor 27 FT-IR spectrometer with Hyperion 1000 attenuated total reflection (ATR) spectroscopy accessory. The thermal stabilities of the samples were measured in a thermo-gravimetric analysis

(TGA, TA instruments, Q-500) with a heating rate of 10 °C min^{-1} under an air flow rate of 60 $ml\ min^{-1}$ from 25 to 700 °C. The magnetic properties of covered samples were recorded at room temperature in a 9T physical properties measurement system (PPMS) by Quantum Design and the conditions which give magnetically harder covering were obtained. The volume resistivity (ρ) of covered samples was measured with a resistivity cell (HP Agilent 16008B) satisfying insulation measurement standard ASTM D-257.

Results and Discussion

The SEM micrographs and FT-IR spectrum of NPs silanized sample are given in Figure 1(a), (b) and (c), respectively. NPs are clearly observed on fiber surface without agglomeration. In the FT-IR spectrum, O-H bending (ca. 3329-3265 cm^{-1}) and C=O bending peaks (ca. 1627 cm^{-1}) of uncovered sample disappear and C-H stretching (ca. 2948-2846 cm^{-1}) and C-H bending peaks (ca. 1452 cm^{-1} and 1375 cm^{-1}) sharpen with higher absorbance and Si-O and Si-O-Metal peaks appear around 971 cm^{-1} and 839 cm^{-1} after silanization. This proves that carbon coated NPs were chemically bonded to cotton via Si-O-Si and C-H bonds along with NPs observed on several washed fabric at SEM image

Compared with the SEM images of 0.02 M PANI coated sample, Figure 2(a) and (b), 0.5 M PANI coated samples reveal that low amount of PANI exhibited random particle settlements on fiber surface, however it established larger patches, bearing as film-like structure as the amount of PANI increased. When PANI polymerization was completed after NPs silanization, Figure 2(c), coating has not been disturbed from NPs and rougher surface defined in Figure 2(b) seems to be avoided.

In the FT-IR spectrum of 0.5 M PANI coated sample, Figure 3, the peaks at 1471 cm^{-1} and 1554 cm^{-1} correspond to the C=C stretching of quinoid ring (Q) and benzene ring (B), respectively with good agreement with early spectroscopic characterization of PANI [27,28]. The peaks at 1290 cm^{-1} and 1232 cm^{-1} are related to the C-N stretching of aromatic amine. The pale peak at around 2902 cm^{-1} is assigned to the aromatic C-H stretching. The peaks at around 1138 cm^{-1} , 971 cm^{-1} and 790 cm^{-1} are due to aromatic C-H in-plane bending, while the peaks at 1108 cm^{-1} and 1647 cm^{-1} are contributed to N=Q=N vibration and C=N vibration from Q group [29]. These characteristics peak show that cotton fabric was successfully coated with PANI via polymerization.

The FT-IR spectrum of PANI/Co@C NP PNC coated sample, Figure 4, shows similar peaks with only PANI coated sample which means that PANI peaks overlap NP peaks, where the band at 2890 cm^{-1} corresponding to C-H stretching shows higher absorbance.

The TGA curves, Figure 5, show that there were two-stage weight losses for the untreated cotton sample at around 350 °

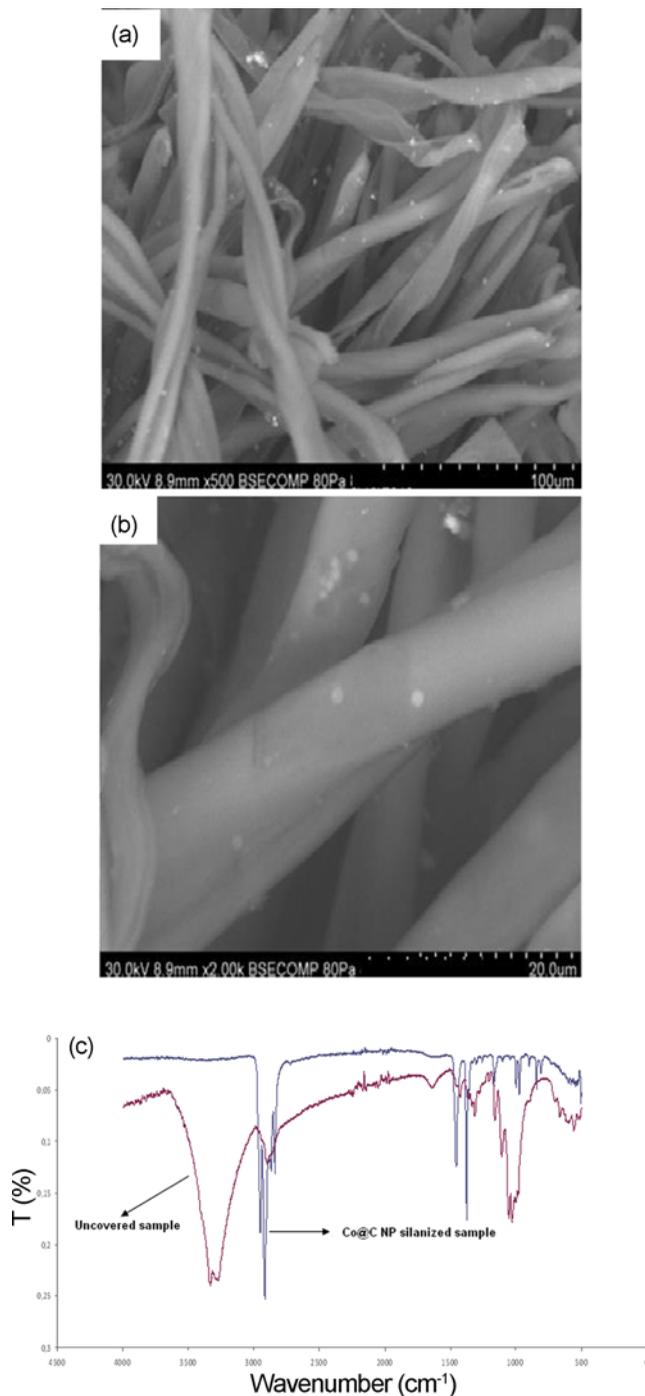


Figure 1. SEM images (a) of Co@C NP (b) of Fe@C NP and FT-IR spectra (c) of Co@C NP silanized sample.

and 560 °C. The NPs (here Co@C) increased decomposition temperature (to 375 °C) with single-stage and residual at higher temperatures was bigger which corresponds to enhanced thermal stability. PANI coated sample degraded faster at lower temperature as a sign of early polymer degradation but the residual (final stability) was still bigger showing also

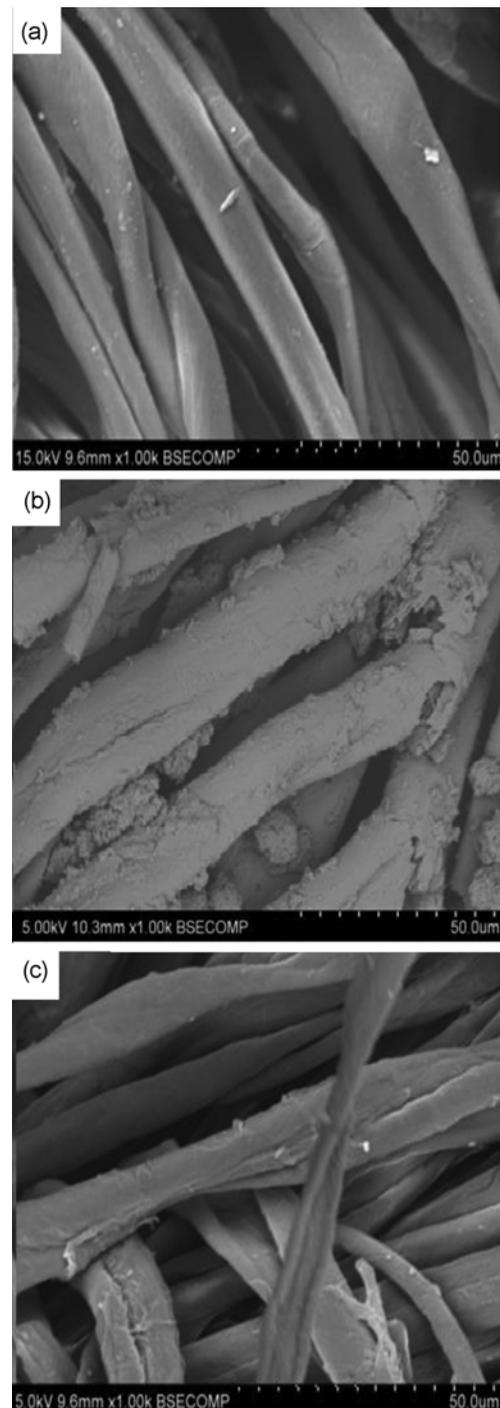


Figure 2. SEM images (a) of 0.02 M PANI (b) of 0.5 M PANI (c) of 0.5 M PANI/Co@C NP PNC coated sample.

enhanced thermal stability. NPs avoided early degradation of PANI when coated with PANI together as sign of thermal stability enhancement. Many groups have reported the thermal stability enhancement effect of nanoparticles in polymeric composites [29-32] and the similar effect was observed for metal NPs on the cotton.

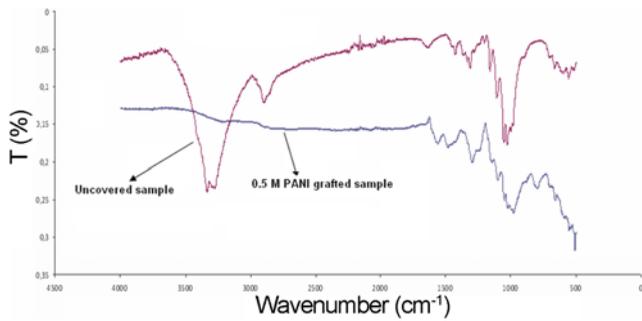


Figure 3. FT-IR spectra of 0.5 M PANI coated sample.

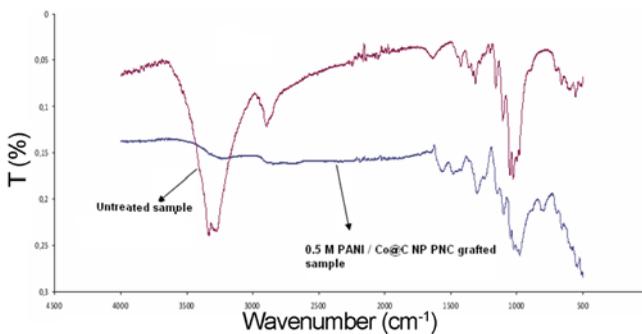


Figure 4. FT-IR spectra of 0.5 M PANI/Co@C NP PNC coated sample.

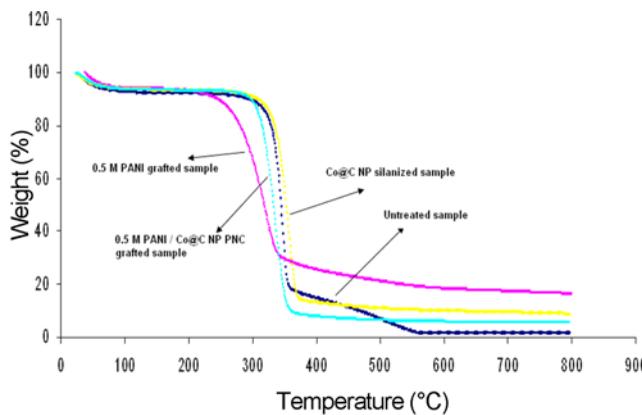


Figure 5. TGA curves of the samples.

Figure 6 shows the room temperature magnetic hysteresis loops. The samples coated with PNCs including Co@C or Fe@C NPs exhibited magnetization; the extrapolated M_r of the samples were 0.024 emu/g and 0.021 emu/g, respectively and the calculated coercivity (H_c) values were almost the same, 240.13 and 240.01 Oe, pointing out the magnetically soft samples. However, sample coated with only PANI, Figure 6(a), did not show magnetic property which is a clear demonstration of PNC effect on magnetization. The contribution of metal NP was found to be non-significant on magnetization and it was concluded that NP amount being same.

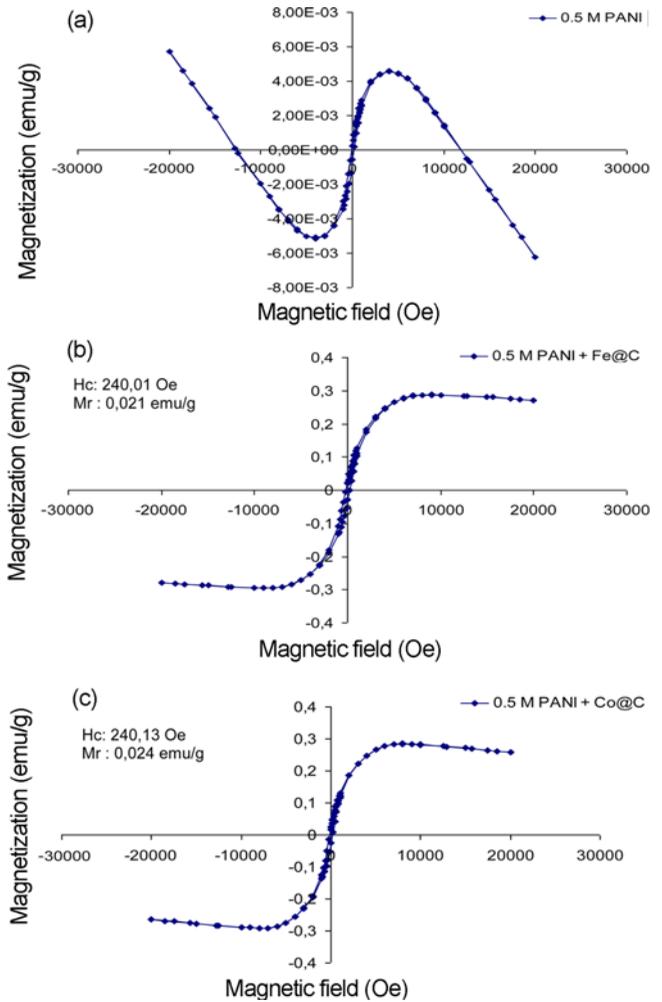


Figure 6. Room temperature magnetic hysteresis loops of (a) 0.5 M PANI coated (b) 0.5 M PANI/Fe@C NP PNC coated (c) 0.5 M PANI/Co@C NP PNC coated samples.

Table 1. Volume resistivity of the samples

| Sample | Volume resistivity (ρ_v) ($\Omega \cdot \text{cm}$) |
|----------------------------|--|
| Untreated | 9.53×10^9 |
| 0.02 M PANI coated | 4.52×10^7 |
| 0.02 M PANI/Co@C NP coated | 3.61×10^7 |
| 0.5 M PANI coated | 5.32×10^4 |
| 0.5 M PANI/Co@C NP coated | 1.56×10^3 |
| 0.5 M PANI/Fe@C NP coated | 1.89×10^3 |

The volume resistivity of the samples, Table 1, were the mean values of four measurements and CV% values of each measurement group were recorded below 3%. The results are also graphed in Figure 7. The results showed the clear decrease in resistivity (increase in electrical conductivity)

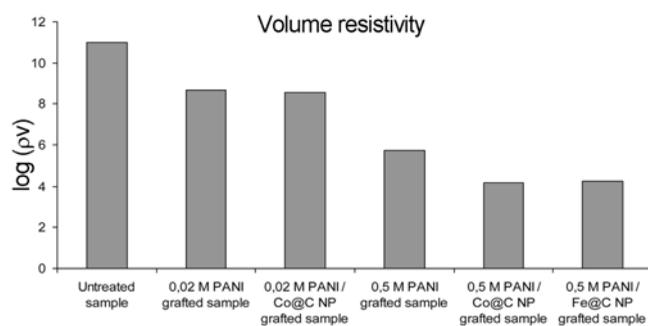


Figure 7. Volume resistivity of the samples.

when comparing coated samples with the untreated one; there was a proportional relation between molar volume of PANI and the conductivity. Also PNCs coating enhanced the conductivity much more than PANI. The different volumes of PANI/metal NP nanocomposites gave also statistically significant volume resistivity values; where 0.5 M PANI/Co@C (or Fe@C) NP PNC coating decreased volume resistivity of fabrics at most (from $9.5 \times 10^9 \Omega \cdot \text{cm}$ to $1.5 \times 10^3 \Omega \cdot \text{cm}$).

Conclusion

This study investigates the electrical conductivity enhancement of cotton samples by conductive polymer (PANI) and PANI/metal nanoparticles (Fe@C and Co@C) composite coating along with chemical characterizations by FTIR, SEM, TGA and PPMS. The results showed that cotton fiber can be successfully grafted by PANI via polymerization where FT-IR pointed the chemical bonding and NPs promoted fine covering without agglomeration. PANI decreased the volume resistivity of cotton fabrics and NPs had an enhancing effect in conductivity which is corresponded to the electrocatalyst performance expected. Also, enhanced thermal stability and magnetization are also justified when PNCs are used. All these findings revealed that PANI/metal NP PNC coated cotton fabrics would exhibit good level electromagnetic shielding performance as a function of combined electrical conductivity and magnetization which is the objective of our future studies.

References

1. T. H. Ueng and K. B. Cheng, *J. Text. Eng.*, **47**, 70 (2001).
2. C. H. Chen, K. C. Lee, J. H. Lin, and M. Koch, *J. Mater. Process. Technol.*, **192-193**, 549 (2007).
3. L. Kessler and W. K. Fisher, *J. Electrostat.*, **39**, 253 (1997).
4. H. G. Ortlek, C. Güneşoğlu, G. Okyay, and Y. Türkoglu, *Tekst. Konfeksiyon*, **2**, 90 (2012).
5. E. Hakansson, A. Kaynak, T. Lin, S. Nahavandi, T. Jones, and E. Hu, *Synth. Met.*, **144**, 21 (2004).
6. S. K. Dhawan, N. Singh, and S. Venkatachalam, *Synth.*

- Met.*, **125**, 389 (2002).
7. S. Kutanis, M. Karakısla, U. Akbulut, and M. Sacak, *Compos. Pt. A-Appl. Sci. Manuf.*, **38**, 609 (2007).
8. E. Cetin, M. Karakısla, and M. Sacak, *Fiber. Polym.*, **9**, 255 (2008).
9. M. Trchova, P. Matějka, J. Brodinová, A. Kalendová, J. Prokeš, and J. Stejskal, *Polym. Degrad. Stabil.*, **91**, 114 (2006).
10. P. C. Rodrigues, M. P. Cantao, P. Janissek, P. C. N. Scarpa, A. L. Mathias, L. P. Ramos, and M. A. B. Gomes, *Eur. Polym. J.*, **38**, 2213 (2002).
11. N. Blinova, J. Stejskal, M. Trchova, and J. Prokes, *Polymer*, **47**, 4248 (2006).
12. C. Zhou, J. Han, G. Song, and R. Guo, *Eur. Polym. J.*, **44**, 2850 (2008).
13. T. Taka, *Synth. Met.*, **41**, 1177 (1991).
14. F. G. Souza, B. G. Soares, and J. C. Pinto, *Macromol. Mater. Eng.*, **291**, 463 (2006).
15. J. Anand, S. Palaniappan, and D. N. Sathyanarayana, *Prog. Polym. Sci.*, **23**, 993 (1998).
16. W. Jia, R. Tchoudakov, E. Segal, M. Narkis, and A. Siegmund, *Synth. Met.*, **132**, 269 (2003).
17. S. Wilson, R. P. J. Jourdain, Q. Zhang, R. A. Dorey, C. R. Bowen, M. Willander, Q. Ul Wahab, M. Willander, S.M. Al-hilli, O. Nur, E. Quandt, C. Johansson, E. Pagounis, M. Kohl, J. Matovic, B. Samel, W. Van der Wijngaart, E. W. H. Jager, D. Carlsson, Z. Djinovic, and M. Wegener, *Mater. Sci. Eng., R*, **56**, 1129 (2007).
18. J. A. Smith, M. Josowicz, M. Engelhard, D. R. Baer, and J. Janata, *Phys. Chem. Chem. Phys.*, **7**, 3619 (2005).
19. J. A. Smith, M. Josowicz, and J. Janata, *Phys. Chem. Chem. Phys.*, **7**, 3614 (2005).
20. P. Kishore, B. Viswanathan, and T. Varadarajan, *Nanoscale Res. Lett.*, **3**, 14 (2007).
21. X. Lu, W. Zhang, C. Wang, T. C. Wen, and Y. Wei, *Prog. Polym. Sci.*, **36**, 671 (2011).
22. K. R. Reddy, K. P. Lee, Y. Lee, and A. I. Gopalan, *Mater. Lett.*, **62**, 1815 (2008).
23. M. Carmo, T. Roepke, C. Roth, A. M. D. Santos, J. G. R. Poco, and M. Linardi, *J. Power Sources*, **191**, 330 (2009).
24. G. Hongbo, Y. Huang, X. Zhang, Q. Wang, J. Zhu, L. Shao, N. Haldolaarachchige, D. P. Young, S. Wei, and Z. Guo, *Polymer*, **53**, 801 (2012).
25. U. A. Sevil, O. Guven, O. Birer, and S. Suzer, *Synth. Met.*, **110**, 175 (2000).
26. S. Radhakrishnan, R. Muthukannan, U. Kamatchi, C. R. K. Rao, and M. Vijayan, *Indian J. Chem.*, **50A**, 970 (2011).
27. J. Zhu, S. Wei, L. Zhang, Y. Mao, J. Ryu, A. B. Karki, D. P. Young, and Z. Guo, *J. Math. Chem.*, **21**, 342 (2011).
28. M. Trchova, P. Matějka, J. Brodinová, A. Kalendová, J. Prokeš, and J. Stejskal, *Polym. Degrad. Stabil.*, **91**, 114 (2006).
29. P. C. Rodrigues, P. R. Janissek, and A. L. Mathias, *Eur. Polym. J.*, **38**, 2213 (2002).

30. M. Xiao, L. Sun, J. Liu, Y. Li, and K. Gong, *Polymer*, **43**, 2245 (2002).
31. B. N. Jang and C. A. Wilkie, *Polymer*, **46**, 2933 (2005).
32. X. Chen, S. Wei, C. Gunesoglu, J. Zhu, C. S. Southworth, L. Sun, A. B. Karki, D. P. Young, and Z. Guo, *Macromol. Chem. Phys.*, **211**, 1775 (2010).