A study on the electrospinning behaviour and nanofibre morphology of anionically charged lignin

Makoto Schreiber[1,3,4], Singaravelu Vivekanandhan[1,2], Amar Kumar Mohanty[1,2], Manjusri Misra[1,2,*]

[1]*Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Guelph, N1G 2W1, ON, Canada*
[2]*School of Engineering, University of Guelph, Guelph, N1G 2W1, ON, Canada*
[3]*Department of Physics, University of Guelph, Guelph, N1G 2W1, ON, Canada*
[4]*Department of Chemistry, University of Guelph, Guelph, N1G 2W1, ON, Canada*

*Corresponding author: E-mail: mmisra@uoguelph.ca

ABSTRACT

The electrospinnability of anionically charged sodium carbonate lignin using positive-voltage electrospinning was explored. The lignin was mixed with polyethylene oxide (PEO) in order to enhance the electrospinning performance by improving the viscoelastic properties. Lignin fibres containing varying concentrations of lignin were obtained by employing various applied voltages. The effect of increased lignin content on the electrospinning behaviour and the obtained fibre morphologies were observed. The electrospun fibres were characterised using scanning electron microscopy (SEM) to investigate their microstructure. SEM analysis showed the formation of well defined lignin fibres and the results indicate that the morphologies are highly depend on the PEO:lignin composition.

Keywords: Lignin; electrospinning; beading; net charge density; carbon fibres; viscosity; SEM.

Makoto Schreiber is currently a 3rd year Nanoscience student in the Department Physics at the University of Guelph. He was the recipient of a University of Guelph Entrance Scholarship and was awarded an Undergraduate Student Research Awards by NSERC. His current research involves the electrospinning of lignin for applications as carbon fibres.

Singaravelu Vivekanandhan is a research scientist at Bioproducts Discovery and Development Centre (BDDC), at the University of Guelph. He received his doctorate degree in physics from Pondicherry University, India in 2007. He has been working on the development of surface enhanced nanostructured materials. He has published 17 peer-reviewed research papers and 2 book chapters including a magazine article.

Amar K. Mohanty is a professor and the Premier's Research Chair in Biomaterials and Transportation, as well as the Director of the Bioproducts Discovery and Development Centre (BDDC), at the University of Guelph. He has more than 450 publications to his credit, including 195 peer-reviewed journal papers, two edited books, 11 book chapters, and 12 U.S. patents; is the honorary editor of the journal Advanced Materials Letters; and is the editor-in-chief of the Journal of Biobased Materials and Bioenergy.

Manju Misra is an associate professor in the School of Engineering and holds a joint appointment in the Dept. of Plant Agriculture at the Univ. of Guelph. Her current research focuses primarily on novel bio-based composite and nanocomposite materials from agricultural and forestry resources for the sustainable bio-economy. She has authored more than 250 publications, including 125 peer-reviewed journal papers, 9 book chapters, and ten U.S. patents; served as an editor of 2 books; is an associate editor of the journal Advanced Science Letters; and is a member of the editorial board of the Journal of Biobased Materials and Bioenergy.

Introduction

Carbon fibres possess many important properties such as a very high specific strength and modulus, good electrical conductivity, good thermal conductivity, a low thermal expansion coefficient, light weight, and enhanced electromagnetic shielding [1, 2]. Thus, they have been used in numerous high performance applications. These include polymer composites (aerospace, marine, medical, civil engineering), alternative energy technologies (lithium ion batteries, supercapacitors, fuel cells), catalysis, filtration (liquid, gas, mixture separation), and storage (hydrogen gas and natural gas) [1, 3-16]. In general, carbon fibres are produced using various precursors such as polyacrylonitrile (PAN), rayon, petroleum pitch, and heterocyclic/non-heterocyclic polymers [5]. The properties of the carbon fibres are highly influenced by the physicochemical properties of the precursor materials. For example, PAN based carbon fibres generally possess higher compressive and tensile strengths compared to pitch based carbon fibres due to a higher structural orientation [5]. Pitch based carbon fibres have greater thermal conductivity than rayon based carbon fibres [5]. However, with current concerns about depleting petroleum resources and their negative environmental impacts, there is a need for alternate resources that could replace or supplement existing petroleum based products [17].

Extensive research has been carried out towards the search of novel renewable resources for the fabrication of carbonaceous materials such as carbon fibres, graphene sheets, carbon nanotubes, activated carbon, and fullerenes [18-24]. The renewable resources used for the fabrication of these carbonaceous materials include plant oils, grasses, plant and animal waste, wood, and lignin [19-21, 25]. Among these, lignin is an efficient precursor for the fabrication of carbonaceous materials due to (i) a carbon rich aromatic structure [26] which results in high carbon yield [27], (ii) a high chemical compatibility [28], (iii) its abundance in nature [26], and (iv) its low cost [26]. Hence, it has been used for the synthesis of different carbon-based materials such as activated carbon, carbon nanostructures, and carbon fibres [21, 29, 30]. For carbon fibre production especially, lignin is found to be a suitable precursor as the stabilization of raw lignin fibres can be performed using lower temperatures and shorter time periods. This can be achieved due the presence of oxygen containing radicals in lignin which facilitate crosslinking reactions [27].

Lignin derived carbon fibres were first produced by Nippon Kayaku Co. by dry spinning an aqueous alkane solution of lignin [26]. Subsequently, many more studies have reported the successful production of lignin based carbon fibres [14, 31-33]. Carbon fibres made from lignin are typically produced by conventional spinning methods such as melt, dry, and fusion spinning [14, 26, 27, 32, 33]. However, these methods can only produce fibres with micrometer scale diameters. The mechanical and other functional properties of carbon fibres increase with the reduction of fibre diameter [34, 29]. Higher quality carbon fibres could be produced by reduction of the precursor fibre diameter [29]. Electrospinning is a simple and versatile method for the fabrication of sub-micron to nanometer diameter fibrous materials. Electrospinning utilises electrostatic interactions to produce continuous fibres from a polymer melt or solution [35, 36]. This has already proven itself as a cheap and simple method to produce PAN based fibres for the fabrication of continuous carbon fibres [29]. So far, there have been few publications on using electrospinning to create lignin based carbon fibre precursors. The existing publications have required the electrospinning process to be facilitated by either mixing lignin with various synthetic polymers [37] or by employing coaxial electrospinning [38].

Depending on the type of lignin used, different types of solvents such as ethanol, dimethylformamide, or water are required to prepare the electrospinning solution [37, 38]. In order to create truly green carbon fibres, the solvent used should also be considered. Therefore, electrospinning water-soluble lignin into carbon fibre precursors would be one of the most environmentally friendly ways to produce carbon fibres. One type of water-soluble lignin is sodium carbonate lignin which is obtained as a waste product from the pulp and paper industry. Hence, the present study explores the feasibility of electrospinning this sodium carbonate lignin into lignin fibres by employing a conventional positive-voltage electrospinning setup. As electrospinning pure lignin solutions has proven difficult, the goal is to produce high-quality lignin fibres with the smallest possible amount of added synthetic polymers. A systematic approach was used to investigate the effects of lignin addition to a polyethylene oxide (PEO) solution on the electrospinning performance.

Experimental

Materials

PEO of 200,000 molecular weight (Mw) and 5,000,000 Mw was purchased from Sigma-Aldrich and used as-received without further purification. Polybind 300 (water-soluble sodium carbonate lignin with strong anionic charges) was purchased from Northway Lignin Chemical. Before use, the lignin was dried in a 100°C laboratory hot air oven until dry. The dry weight of the lignin was ~50% of the as-received wet lignin weight. Deionized water was used as the common solvent for both PEO and lignin.

Preparation of PEO/lignin solutions

PEO stock solution was made by adding 4% (weight by volume) of a mixture of 200,000 and 5,000,000 Mw PEO in an 85:15 ratio into water. This ratio was optimised based on electrospinning data for their individual components representing various viscoelastic behaviours and electrospinning voltage ranges. Various amounts of dried lignin was added to the PEO solutions to make solutions containing 0, 10, 20, 30, 40, 50, 60, 70, 80 90, and 100% lignin (relative to PEO mass). The solutions were prepared by mixing them at room temperature under constant stirring until the components were completely dissolved. The PEO mixtures with different formulations are shown in **Fig. 1**. Prior to electrospinning, the viscosities of the obtained solutions were measured using a Brookfield DV-II+ Pro

viscometer at room temperature and the values are reported in **Fig. 2.**

Fig. 1. From left to right, the prepared 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100% lignin solutions.
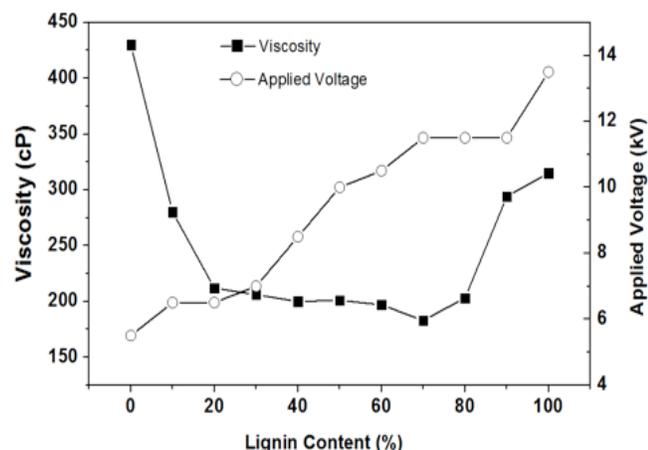
Fig. 2. The change in solution viscosity with increasing lignin content and the applied voltage used to electrospin each solution.

Electrospinning of PEO/lignin fibres

Electrospinning was performed in a NANON-01A electrospinning setup, MECC Co., Ltd. Japan. A custom made sample collector was employed to achieve a suitable working distance. 2 ml of each solution were electrospun using a 24 gauge needle, a flow rate of 0.1 ml/h, and a working distance of 22.5 cm. The chamber temperature and relative humidity (Rh) varied from 22-27°C and 42-67% respectively. The electrospinning voltage was varied from 5.5 kV to 13.5 kV depending on the lignin concentration as shown in **Fig. 2**. During the electrospinning process, the length of the stable region of the jet (where the jet appears to be stationary) was measured with a ruler. After electrospinning, the fibre samples of were stored inside a desiccator to prevent moisture adsorption.

Characterization of PEO/lignin fibres

The morphologies of the PEO/lignin fibres were analysed using an FEI - Inspect S50 scanning electron microscope (SEM). The fibres were sputter coated with ~20 nm of gold particles in order to enhance the image acquisition. The obtained SEM images were further analysed using the ImageJ software to measure the fibre diameters.

Results and discussion

The effect of lignin content on solution viscosity

The effects of lignin content on the PEO/lignin solution viscosities was recorded and presented in **Fig. 2**. In **Fig. 2**, it is clearly shown that as the lignin content was increased to 40% in the PEO solutions, the solution viscosities decreased. Afterwards, the viscosities remained relatively constant up to 80%. Further addition of lignin (90-100%) caused an increase in the viscosities. In accordance with Goring's study [**39**], the initial viscosity loss is justified due to the low intrinsic viscosity that the lignin imparts to solutions. The sudden increase in viscosity at higher lignin concentrations is likely due to the solution becoming saturated and increasing the amount of hydrogen bonding between the lignin chains. Thus, the mobility of the polymers within the solution is decreased and the viscosity increases. The saturation of the solution also causes a higher density of lignin molecules per unit volume. In each case, the solutions containing lignin all possessed lower viscosity values than either that of the pure PEO solution or that of the as-received lignin solution (1000 cP). This is because the prepared solutions were all at a much lower polymer concentrations in water compared to the as-received lignin.

Electrospinnability of PEO/lignin solutions

As the lignin content of the solutions was increased, the stable region of the electrospinning jet gradually became shorter. The stable region was initially about 5 cm in length at 0% lignin. With the addition of 10% lignin, the stable region's length decreased to about 3 cm and gradually decreased to about 1 cm with increasing lignin content. At 90% lignin, the stable region almost disappeared, being only about 0.2 cm long. This corresponds to the point at which the viscosity suddenly increases. It was observed that an increasingly higher applied voltage (on average a 0.5 kV increase for each 10% increase in lignin content) was required to initiate a stable electrospinning jet as the lignin content was increased (**Fig. 2**). A likely cause for this is that as the lignin content in the solution was increased, the anionic charge of the solution also increased. This anionic charge neutralized some of the positive charges applied by the high-voltage power supply (HVPS). Therefore, to build up enough charge on the solution droplet to initiate an electrospinning jet, a higher applied voltage was required.

Interestingly, electrospinning of PEO/lignin solution with 80-100% lignin caused the formation of floating fibres that rose up from the collector as shown in **Fig. 3**. At 90 and 100% lignin, all the fibres were floating fibres and no fibre mat was formed on the collector. It was also observed that the floating fibres were attracted towards the electrospinning needle and seemed to repel each other. If the applied voltage was stopped, the floating fibres would collapse onto the collector. Between 80-100% lignin, the increased lignin density in solution causes a sudden increase in the charge density of the resulting fibres. As the floating fibres are attracted towards the positively charged

needle, they must be negatively charged and have a net charge density (NCD) large enough that the electrical attraction between the needle and the floating fibres overcomes the gravitational force on the fibres.

The effect of lignin content on fibre morphology

SEM analysis was performed in order to identify the morphology of electrospun fibres with different lignin concentrations as shown in **Fig. 4**. The fibres made with 0% lignin (pure PEO) (**Fig. 4i**) exhibit smooth and defect free morphologies with fibre diameters of ~400nm. When lignin was blended into PEO solution from 10-30% (**Fig. 4ii-iv**), the fibres started to show bead defects which became more numerous with increasing lignin content. Addition of lignin also caused the reduction of fibre diameter which was observed as ~300nm for the 10-30% lignin fibres. This reduction in diameter may partially be due to the drop in viscosity which makes the fibres easier to stretch while spinning. When the lignin content was increased to 40% (**Fig. 4v**), a dramatic increase in beading was observed in which the fibres are composed almost entirely of beads. Further addition of lignin from 50-70% (**Fig. 4vi-viii**) gradually decreased the amount of beading on the fibres and an improved fibre structure was observed at the lignin content of 80% (**Fig. 4ix**). At this stage, the fibre diameters are found to be ~150nm. At higher lignin contents of 90-100% (**Fig. 4x-xi**), the formation of thicker fibres with large variations in fibre diameter were observed. These fibres showed a high tendency to fuse into bundles.

Fig. 3. The large floating fibre (indicated by arrow) which is surrounded by smaller floating fibres (indicated by the circle). The fibres are on the collector and the electrospinning needle is above the image.

This strange trend in the beading patterns of the fibres is most likely due to changes in the NCD of the electrospinning jet. As the lignin content was increased, the solution's inherent negative charge was also increased. This negative charge neutralizes some of the positive charges applied by the HVPS and results in a reduction of the NCD of the electrospinning jet. As was reported by Fong et al., decreasing NCD increases bead formation [**40**]. The drop in the solution viscosities may also have contributed to the increased incidences of beading. At 40% lignin (**Fig. 4v**), the sudden dominance of beads suggests that the positive and negative charges in the electrospinning jet are roughly equal, making the NCD of the jet approach zero. From 50-80% lignin (**Fig. 4vi-ix**), the amount of beading is decreasing as the magnitude of the NCD of the electrospinning jet is now increasing with a negative polarity.
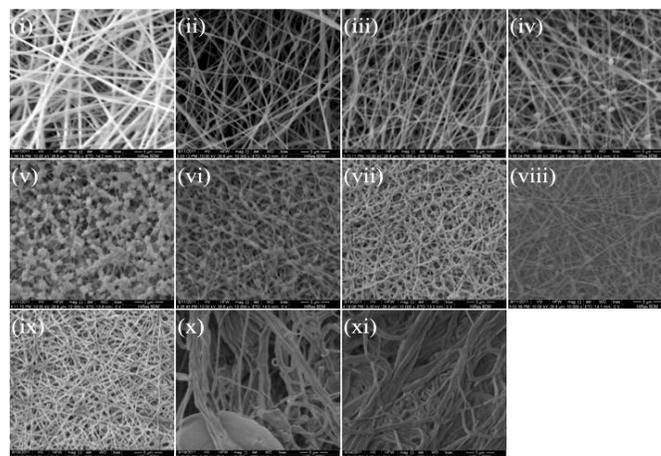
Fig. 4. Scanning electron microscopy images of electrospun fibres with increasing lignin content. (i) 0%, (ii) 10%, (iii) 20%, (iv) 30%, (v) 40%, (vi) 50%, (vii) 60%, (viii) 70%, (ix) 80%, (x) 90%, (xi) 100%. All scale bars = 5μm.

Conclusion

The fabrication of lignin fibres from anionically charged sodium carbonate lignin using the electrospinning process was demonstrated. PEO played a vital role in facilitating the electrospinnability of lignin by improving the viscoelastic nature of the precursor solution. Addition of lignin to the PEO solution affected the viscosity of the solution, the electrospinning behaviour of the solution, and the resultant fibre morphology. An improved lignin fibre structure was observed for the 80% lignin to PEO mass solution and the obtained fibres were found to be ~150nm in diameter. Increasing lignin content in the precursor solution makes the electrospinning process increasingly unstable due to charge neutralization between the positive charges applied by the HVPS and the anionic charges on the lignin. The charge interactions also affected the amount of beading on the resultant fibres. Employing negative-voltage electrospinning instead of the conventional positive-voltage electrospinning may improve the electrospinnability of sodium carbonate lignin due to the applied charges superimposing with the lignin's inherent charges instead of neutralizing them.

Acknowledgements

Reference

1. Chand, S. *J. Mater. Sci.* **2000**, *35*, 1303.
   DOI: 10.1023/A:1004780301489
2. Dasa, N.C.; Khastgira, D.; Chakia, T.K.; Chakraborty, A. *Composites, Part A* **2000**, *31*, 1069.
   DOI: 10.1016/S1359-835X(00)00064-6
3. Park, S.B.; Lee, B.I.; Lim, Y.S. *Cem. Concr. Res.* **1991**, *21*, 589.
   DOI: 10.1016/0008-8846(91)90110-4
4. Ryu, Z.; Zheng, J.; Wang, M.; Zhang, B. *J. Colloid Interface Sci.* **2000**, *230*, 312.
   DOI: 10.1006/jcis.2000.7078
5. Thiruvenkatachari, R.; Su, S.; An, H.; Yu, X. X. *Prog. Energy Combust. Sci.* **2009**, *35*, 438.
   DOI: 10.1016/j.pecs.2009.05.003
6. Matsuo, T. *Text. Prog.* **2008**, *40*, 87.
   DOI: 10.1080/00405160802133028
7. Burchell, T. *Oak Ridge National Laboratory* **2001**.
   WEB: http://www.ornl.gov/~webworks/cppr/y2001/misc/114925.pdf
8. Yusof N.; Ismail A. F. *International Journal of Chemical and Environmental Engineering* **2010**, *1*, 79.
9. Suarez-Garcia, F.; Vilaplana-Ortego, E.; Kunowsky, M.; Kimura, M.; Oya, A.; Linares-Solano, A. *Int. J. Hydrogen Energy* **2009**, *34*, 9141.
   DOI: 10.1016/j.ijhydene.2009.09.026
10. Jenkins, D.H. *The Journal of Bone and Joint Surgery* **1978**, *60*, 520.
11. . Williams, G.; Trask, R.; Bond, I. *Composites, Part A* **2007**, *38*, 1525.
    DOI: 10.1016/j.compositesa.2007.01.013
12. Summerscales, J.; Short, D. *Composites* **1978**, *9*, 157.
    DOI: 10.1016/0010-4361(78)90341-5
13. Lancaster, J.K. *Wear* **1972**, *20*, 315.
    DOI: 10.1016/0043-1648(72)90413-9
14. Pandolfo, A.G.; Hollenkamp, A.F. *J. Power Sources* **2006**, *157*, 11.
    DOI: 10.1016/j.jpowsour.2006.02.065
15. Yazami, R.; Zaghib, K.; Deschamps, M. *J. Power Sources* **1994**, *52*, 55.
    DOI: 10.1016/0378-7753(94)01933-9
16. Dicks, A. L. *J. Power Sources* **2006**, *156*, 128.
    DOI: 10.1016/j.jpowsour.2006.02.054
17. Hill, J.; Nelson, E.; Tilman, D.; Polasky, S.; Tiffany, D. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 11206.
    DOI: 10.1073/pnas.0604600103
18. Kubo, S.; Uraki, Y.; Sano, Y. *Carbon* **1998**, *36*, 1119.
    DOI: 10.1016/S0008-6223(98)00086-4
19. Ruan, G.; Sun, Z.; Peng, Z.; Tour, J. M. *ACS Nano* **2011**, *5*, 7601.
    DOI: 10.1021/nn202625c
20. Kang, Z.; Wang, E.; Mao, B.; Su, Z.; Chen, L.; Xu, L. *Nanotechnology* **2005**, *16*, 1192.
    DOI: 10.1088/0957-4484/16/8/036
21. Hayashi, J.; Kazehaya, A.; Muroyama, K.; Watkinson, A. P. *Carbon* **2000**, *38*, 1873.
    DOI: 10.1016/S0008-6223(00)00027-0
22. Uçar, S.; Erdem, M.; Tay, T.; Karagöz, S. *Appl. Surf. Sci.* **2009**, *255*, 8890.
    DOI: 10.1016/j.apsusc.2009.06.080
23. Özdemir, M.; Bolgaz, T.; Saka, C.; Şahin, O. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 171.
    DOI: 10.1016/j.jaap.2011.05.010
24. Hata, T.; Imamura, Y.; Kobayashi, E.; Yamane, K.; Kikuchi, K. *J. Wood Sci.* **2000**, *46*, 89.
    DOI: 10.1007/BF00779560
25. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1788.
    DOI: 10.1039/B703294C
26. Compere, A. L.; Griffith, W. L.;. Leitten, C. F Shaffer, J. T. *Oak Ridge National Laboratory* **2001**.
    WEB: http://www.ornl.gov/~webworks/cppr/y2001/pres/111380.pdf
27. Davé, V.; Prasad, A.; Marand, H.; Glasser, W. G. *Polymer* **1993**, *34*, 3144.
    DOI: 10.1016/0032-3861(93)90382-K
28. Lewis, N.G.; Lantzy, T. R. *ACS Symp. Ser.* **1989**, *385*, 13.
    DOI: 10.1021/bk-1989-0385.ch002
29. Liu, C.; Lai, K.; Liu, W.; Yao, M.; Sun, R. *Polym. Int.* **2009**, *58*, 1341.
    DOI: 10.1002/pi.2669
30. Misra, M.; Vivekanandhan, S.; Sahoo, S.; Mohanty, A. K. *CIPET TIMES* January - April 2010.
    WEB: http://cipet.gov.in/pdfs/CIPET_TIMES_jan-april-2010.pdf
31. Kadla, J. F.; Kubo, S.; Venditti, R.A.; Gilbert, R.D.; Compere, A.L.; Griffith, W. *Carbon* **2002**, *40*, 2913.
    DOI: 10.1016/S0008-6223(02)00248-8
32. Sudo, K.; Shimizu, K. *J. Appl. Polym. Sci.* **1992**, *44*, 127.
    DOI: 10.1002/app.1992.070440113
33. 33. Sudo, K.; Shimizu, K.; Nakashima, N.; Yokoyama, A. *J. Appl. Polym. Sci.* **1993**, *48*, 1485.
    DOI: 10.1002/app.1993.070480817
34. Tibbetts, G. G.; Beetz, C. P. *J. Phys. D: Appl. Phys.* **1987**, *20*, 292.
    DOI: 10.1088/0022-3727/20/3/008
35. Huang, Z.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
    DOI: 10.1016/S0266-3538(03)00178-7
36. Doshi, J.; Reneker, D. H. *J. Electrost.* **1995**, 35, 151.
    DOI: 10.1016/0304-3886(95)00041-8
37. Dallmeyer, I.; Ko, F.; Kadla, J. F. *Res* **2010**, *30*, 315.
    DOI: 10.1080/02773813.2010.527782
38. 38. Ruiz-Rosas, R.; Bedia, J.; Lallave, M.;. Loscertales, I. G.; Barrero, A.; Rodríguez-Mirasol, J.; Cordero, T. *Carbon* **2010**, *48*, 696.
    DOI: 10.1016/j.carbon.2009.10.014
39. Goring, D. A. I. *Pure Appl. Chem.* **1962**, *5*, 233.
    DOI: 10.1351/pac196205010233
40. Fong, H.; Chun, I.; Reneker, D. H. *Polymer* **1999**, *40*, 4585.
    DOI: 10.1016/S0032-3861(99)00068-3