PREPARATION OF AL₂O₃ COATED PVA AND PVP NANOFIBERS AND AL₂O₃ NANOTUBES BY ELECTROSPINNING AND ATOMIC LAYER DEPOSITION

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One dimensional nanomaterials, nanofibers have attracted great attention in the recent decades due to their excellent chemical, mechanical, electrical, optical and magnetic properties. In this work poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) polymer fibers were prepared by electrospinning from their aqueous solutions. Onto the polymer nanofibers Al₂O₃ layers were deposited by ALD. The film growth of 50 nm thick layers was done at 50 °C, trimethylaluminium (TMA) and water were used as precursors. Consecutively, the polymer core template of the oxide layers was removed to obtain metal oxide nanotubes. The removal took place in two ways: by heating or by dissolution. In order to be able to remove the polymer completely by the annealing process, the thermal properties of the as-prepared polymer nanofibers were analyzed by TG/DTA and the annealing temperature (550 °C) was determined. For the removal of the core from the composite fibers by dissolution, the nanocomposites were immersed in water at 60 °C. The polymer nanofibers, the core/shell nanocomposites and the nanotubes were all investigated by SEM-EDX, XRD and FT-IR methods. The SEM pictures revealed the obtained fibrous structure of the polymers after the electrospinning. It also showed the similar and unchanged fibrous morphology of the nanocomposites after the ALD, and confirmed the as-prepared nanotube mats after the removal of the polymer templates. Based on the XRD results, the Al₂O₃ nanotubes obtained by both template dissolution and by annealing were amorphous. By analyzing the FT-IR spectra, it was concluded that the removal of the templates was successful and pure oxide nanotubes were obtained.
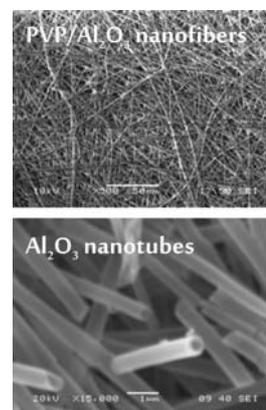
INTRODUCTION

In recent years 1D nanostructures (*e.g.* nanofibers, nanorods, nanotubes) are gaining attention in many different fields due to their excellent physical and chemical properties, which can be precisely controlled by various production methods.[1-3] Among them nanofibers can be used in surgical implants,[4] chemical[5] and biosensors,[6] tissue engineering,[7] drug delivery systems,[8-9] electronic devices,[10-11] water filtration systems, etc.[12]

One of the methods for obtaining nanofibers is electrospinning. Electrospinning is a fiber producing method with uses electric force to draw the threads from the polymer solutions of the materials. When the high voltage is applied to the liquid it becomes charged, and due to the electrostatic repulsion, from the surface charged jets can erupt, which dry during flight, before reaching the grounded collector. With this method nanometer-scale uniform fibers can be produced, which have high specific surface area.[13] With this

technique polymer[14-15] and also polymer/inorganic fibers[16] can be produced.

The fibers synthetized by electrospinning can be used as templates as well in further preparations, *e.g.* thin layers can be deposited onto them by many different techniques. If these fibers are pure polymers, it is important to choose a low temperature deposition method. Atomic layer deposition (ALD), which is a gas phase chemical process for the deposition of thin films, can be a suitable preparation if the appropriate precursors are chosen.[17] In ALD there are 4 steps in one cycle of deposition: (i) first one of the reactants are let into the reactor, which is than chemisorbed on the surface of the sample, (ii) it is followed by an inert gas purge, and (iii) the second precursor is let into the reactor, and (iv) finally an inert gas purge ends the cycle.[18-19] The reaction can only happen between the adsorbed species and thanks to these alternating surface controlled reactions the growth of thin films is possible within nanometer range precision. By combining electrospinning and ALD,[20-21] core/shell nanocomposites with a high variety of properties can be prepared and also by the removal of the core material nanotubes with controlled wall thickness can be produced.

In this work the preparation of polymer/oxide nanocomposites and oxide nanotubes was studied. At first poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) nanofibers were prepared from their aqueous solutions by electrospinning, then 50 nm thick Al_2O_3 films were grown on the polymer templates by ALD from trimethylaluminium and water as precursors at 50°C. The polymer cores were removed by either dissolution or by annealing from the samples and therefore Al_2O_3 nanotubes were obtained. The polymer nanofibers, polymer/oxide core/shell nanocomposites and oxides nanotubes were studied by simultaneous thermogravimetry/differential thermal analysis (TG/DTA), scanning electron microscopy – energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) methods.

EXPERIMENTAL

The polymer nanofibers were prepared from their aqueous solutions by electrospinning. For the PVP solution 1.1 g of PVP was dissolved in 4 mL of distilled water. The solution was stirred for 24 h at room temperature. For the preparation of the PVA fibers 0.4 g of the polymer was dissolved in 4 mL of distilled water and stirred for 4 h at room temperature. The

solutions were transferred into a syringe and connected to polymer tubing with the needle tip at the other end. The 0.5 mL/h feeding rate was controlled by an electric pump. The applied voltage was 20 kV during the electrospinning and an aluminum foil covered with polypropylene fabric was used as the collecting device. The polypropylene fabric was applied, because the fiber mats could easily be removed from them.

In order to determine at what temperature the coating of the fibers could be done without melting the polymers, the thermal properties of the PVA and PVP fibers were analyzed in inert atmosphere (nitrogen, 130 mL/min) by a TA Instruments SDT 2960 simultaneous TG/DTA. The measurements were done also in air (130 mL/min) to determine at what temperature the composite should be heated to remove the polymer core. The polymers were heated up to 600 °C in Pt crucibles with a 10 °C/min heating rate in nitrogen and air as well.

The atomic layer deposition of thin films on the nanofibers was done in a Beneq TFS-200-186 reactor. The Al_2O_3 films were prepared from trimethylaluminium (TMA) and H_2O as precursors. The TMA pulse time was 0.15 s and it was followed by a 0.5 s nitrogen purge. The H_2O pulse time was 0.15 s as well and the purge time was 0.75 s. The 50 nm layers were grown in 400 cycles at 50 °C. Al_2O_3 was grown also on glass substrate under the same conditions, and the theoretical thickness of the layers was confirmed by profilometer.

The removal of the polymer template to obtain Al_2O_3 nanotubes was done with two different methods: dissolution and annealing. PVA and PVP are both water-soluble polymer, thus, the dissolution was done in water at 60 °C for 2 h. The solution could not have been stirred, for the reason that it could have led to the damage of the nanotubes; hence, the solvent was changed every 30 minutes.

The removal of the core by annealing was done in the TA Instruments SDT 2960 simultaneous TG/DTA instrument. The nanocomposites were heated to 230 °C with 10 °C/min, then the heating rate was lowered to 2 °C/min to avoid the breaking and cracking of the oxide walls. The annealing continued till 550 °C with the lower heating rate.

The morphology and the composition of the samples was studied by SEM-EDX analysis with a JEOL JSM-5500LV scanning electron microscope. The measurements were done at 20 kV voltage. Before the measurement the nanocomposites were coated with a thin Au/Pd layer in a sputter coater.

The powder XRD patterns were measured with a PANalytical X'pert Pro MPD X-ray diffractometer using Cu Kα irradiation.

The FT-IR spectra were studied to be able to see whether the polymers were totally removed from the nanocomposites by a Bruker Tensor 37 IR spectrometer equipped with a Goldengate SpecAC ATR head.

RESULTS AND DISCUSSION

The SEM images showed that the as-prepared PVP (Fig. 1/A) and PVA (Fig. 2/A) polymers had a fibrous structure, the samples consisted of more or less uniform and even nanofibers. The thickness of the PVP nanofibers was 500-700 nm, while the PVA fibers were 200-300 nm wide. Both type of fibers were several centimeters long.
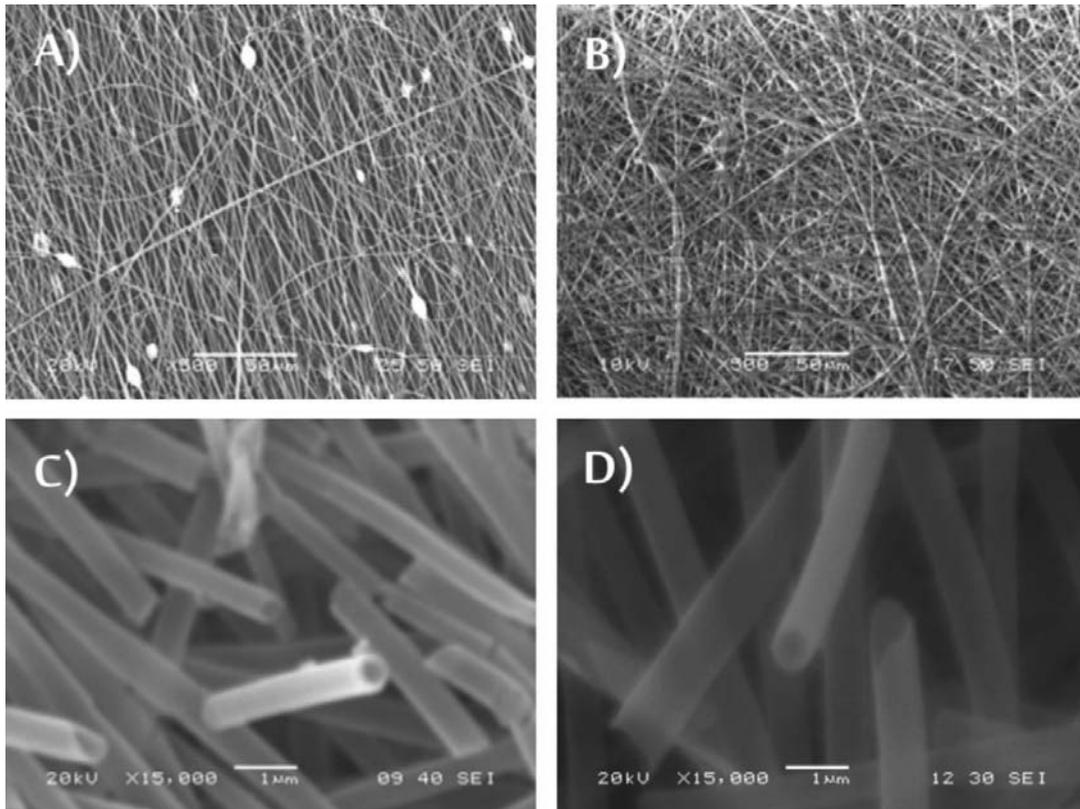
Fig. 1 – SEM images of A) PVP nanofibers B) Al$_2$O$_3$ coated PVP nanofibers C) Al$_2$O$_3$ nanotubes prepared by annealing from PVP/Al$_2$O$_3$ nanocomposite D) Al$_2$O$_3$ nanotubes prepared by dissolution from PVP/Al$_2$O$_3$ nanocomposite.
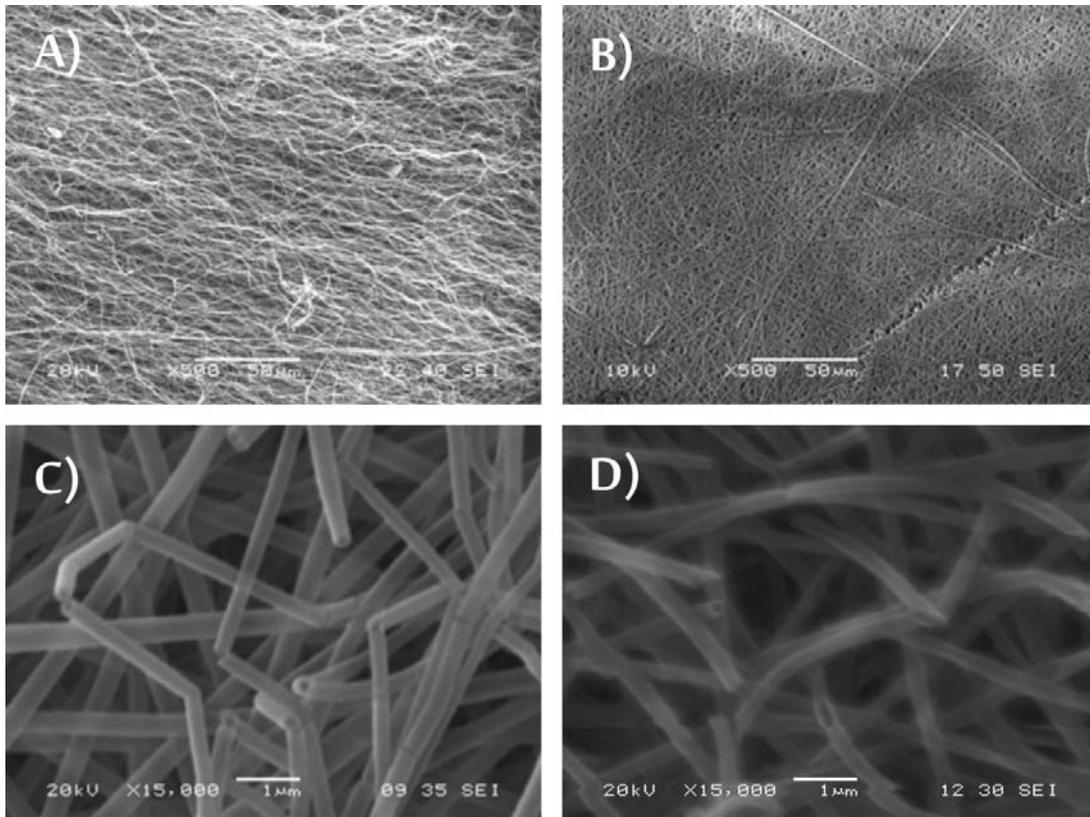
Fig. 2 – SEM images of A) PVA nanofibers B) Al$_2$O$_3$ coated PVA nanofibers C) Al$_2$O$_3$ nanotubes prepared by annealing from PVA/Al$_2$O$_3$ nanocomposite D) Al$_2$O$_3$ nanotubes prepared by dissolution from PVA/Al$_2$O$_3$ nanocomposite.

After their preparation the polymers were investigated by TG/DTA (Fig. 3). In nitrogen atmosphere under 100 °C there was no significant mass loss, only the solvent evaporated from the samples, the decomposition of both the PVP and PVA started above 200 °C. Up to 600 °C the polymers did not decompose totally, and an organic char residue remained. Based on this the ALD decomposition temperature was set to 50 °C. In air the difference was that the decomposition happened in several overlapping steps and the polymers not just decomposed, but were burnt as well. Again in the case of both PVP and PVA, up to 100 °C only the loss of water took place, the decomposition started above 200 °C, at first the decomposition of the functional groups and the side chains happened, then the main chain's at higher temperature.[22-24] At 550 °C the polymers were totally burnt. From these results the heating program was determined for the annealing of the polymer core; at first the samples were heated to 230 °C with 10 °C/min rate, then the heating rate was lowered to 2 °C/min to avoid damaging the nanotube structure, when the most intense gas release and combustion occured. The annealing was finished at 550 °C.
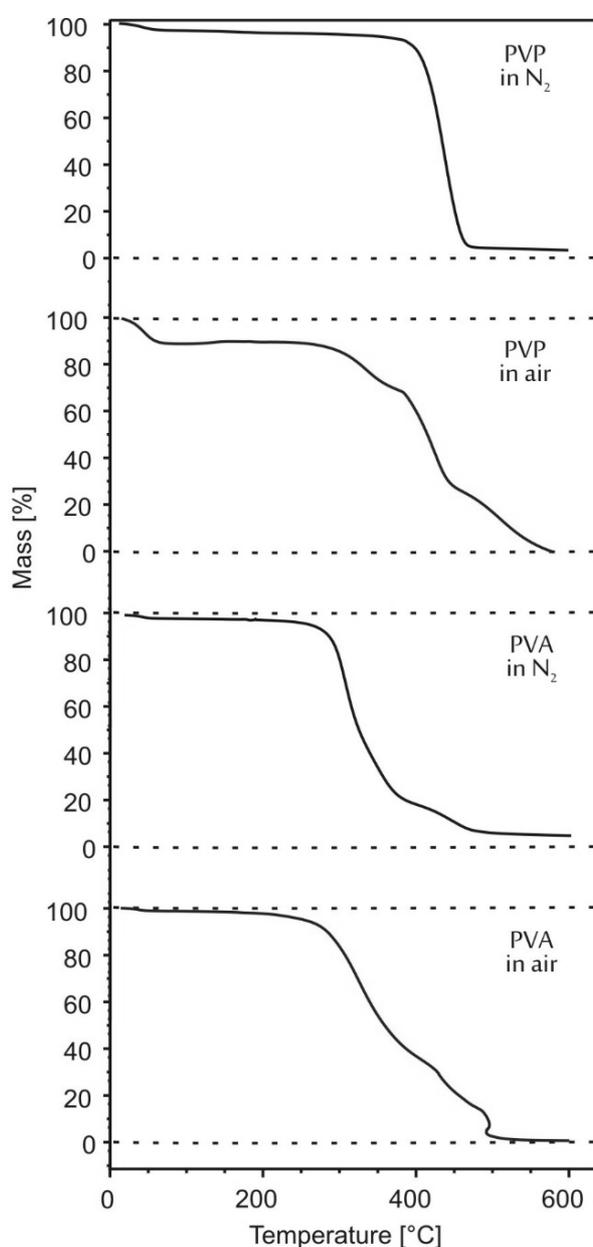
Fig. 3 – TG curves of the PVP and PVA nanofibers in N_2 and air.

Table 1

Results of the SEM-EDX analysis

	Composition (wt%)	
	PVP/Al$_2$O$_3$	PVA/Al$_2$O$_3$
C	19.4	13.1
O	49.3	56.6
N	2.4	-
Al	28.9	30.3
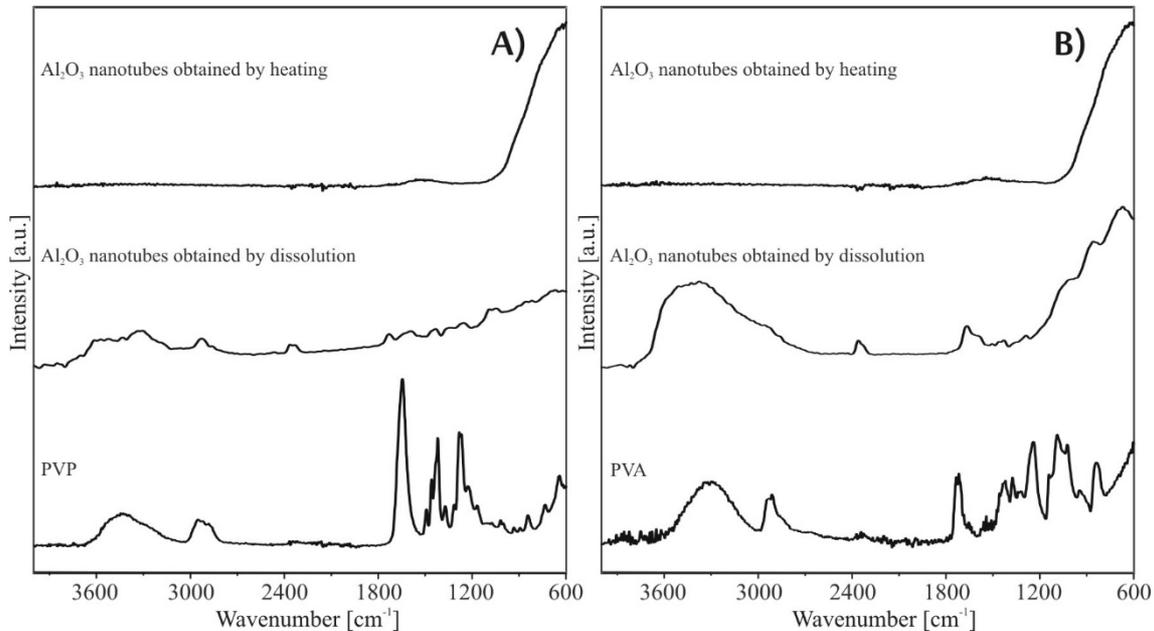
Fig. 4 – FT-IR spectra of the prepared samples, A) PVP nanofibers, Al$_2$O$_3$ nanotubes obtained by dissolution from PVP/Al$_2$O$_3$ nanocomposite, Al$_2$O$_3$ nanotubes obtained by heating from PVP/Al$_2$O$_3$ nanocomposite; B) PVA nanofibers, Al$_2$O$_3$ nanotubes obtained by dissolution from PVA/Al$_2$O$_3$ nanocomposite, Al$_2$O$_3$ nanotubes obtained by heating from PVA/Al$_2$O$_3$ nanocomposite.

After the deposition of Al$_2$O$_3$ by ALD onto the nanofibers were studied by SEM-EDX again, the nanocomposites and also after removing the core by the two different methods, the nanotubes were similarly investigated. On Fig. 1/B and Fig. 2/B it is visible that the polymer/Al$_2$O$_3$ core/shell samples still had a fibrous structure, the polymers did not melt during the ALD thin films growth. The PVP/Al$_2$O$_3$ nanofibers were about 550-750 nm wide, while the PVA/Al$_2$O$_3$ fibers had a diameter of 250-350 nm and both maintained their previous length. The core/shell composite samples contained about 30 wt% aluminum (Table 1). The SEM pictures (Fig. 1/C-D, Fig. 2/C-D) show that the removal of the core was successful by dissolution and by annealing as well, however the nanotubes broke into shorter, few μm long pieces in some places. The inner diameter of the nanotubes was consistent with the width of the polymer cores and the wall thickness was about 50 nm corroborating the profilometer results.

The XRD results revealed that the ALD deposited Al$_2$O$_3$ layers were amorphous, and after

the preparation of oxide nanotubes both by dissolution and by heating, the Al$_2$O$_3$ nanotubes were still amorphous.

Finally, the samples were studied by FT-IR (Fig. 4/A-B) to be able to determine whether the removal of the polymer cores was complete. At first, the spectra of the pure polymers were measured. By both polymers the broad peaks between 3100-3500 cm^{-1} corresponded to the stretching vibration of the OH groups. In the spectrum of the PVP the peaks at 1649 cm^{-1}, 1285 cm^{-1} and 1271 cm^{-1} were the stretching vibrations of the C=O and C-O, C-N bonds respectively, while the bands at 1460 cm^{-1} and 1422 cm^{-1} referred to the bending modes of the CH$_2$ groups.[16,25] In the case of the PVA nanofibers the peaks at 1732 cm^{-1} and 1088 cm^{-1} could be assigned to the C=O bonds. The peaks at 1373 cm^{-1} and 1240 cm^{-1} were the wagging vibrations of the CH$_2$ and CH groups respectively, while the band at 839 cm^{-1} was the C-C stretching mode.[26] From the spectra it is visible that with the dissolution of the PVP and PVA cores, the removal of the polymers

was not absolutely complete, smaller intensity peaks could be found in the spectra that showed the presence of the polymers in the samples, however under 1000 cm^{-1} a broad band of overlapping peaks appeared, which were the lattice vibrations of the Al$_2$O$_3$. When the cores were removed by annealing, on the FT-IR spectra the peaks referring to the polymers disappeared, only the lattice vibrations of the Al$_2$O$_3$ were visible; thus, the PVP and PVA were removed from the nanocomposites without residue.

CONCLUSION

Based on the results, the preparation of the PVP/ Al$_2$O$_3$ and PVA/ Al$_2$O$_3$ core/shell nanofibers was successful, the low temperature ALD deposition did not damage the fibrous structure of the electrospun polymer fibers, they did not melt during the growth of the thin films. Consecutively, the production of amorphous Al$_2$O$_3$ nanotubes was also achieved by the removal of the polymer cores. The SEM images showed the formation of Al$_2$O$_3$ nanotubes by the dissolution and by the annealing as well. The FT-IR measurements proved the annealing process to be more effective for the removal of the polymer templates from the core/shell composites, however, due to the evolving gases it can be more damaging to the structure of the nanotubes. Probably with a longer dissolution time or higher temperature the efficiency of polymer dissolution could be raised.

In summary, the combination of electrospinning and atomic layer deposition is suitable for the preparation of organic/inorganic core/shell nanocomposite fibers and also for the production of oxide nanotubes by the removal of the core. With these methods, the thickness of the deposited layers and the inner diameter of the nanotubes can be precisely controlled.

REFERENCES

1. H. Gleiter, *Acta Mater.*, **2000**, *48*, 1–29.
2. Kenry and C. T. Lim, *Prog. Polym. Sci.*, **2017**, *70*, 1–17.
3. S. Mihaiu, O. C. Mocioiu, A. Toader, I. Atkinson, J. P. Cuşu, C. Munteanu and M. Zaharescu, *Rev. Roum. Chim.*, **2016**, *61*, 485–493.
4. L. Huang, T. Liu, K. Liu and Y. Liu, *J. Nanosci. Nanotechnol.*, **2012**, *12*, 5066–5070.
5. C. Chen, Y. Tang, B. Vlahovic and F. Yan, *Nanoscale Res. Lett.*, **2017**, *12*, 1–15.
6. M. Zhang, X. Zhao, G. Zhang, G. Wei and Z. Su, *J. Mater. Chem. B*, **2017**, *5*, 1699–1711.
7. J. R. Dias, P. L. Granja and P. Jorge, *Int. J. Bioprinting*, **2017**, *3*, 1–8.
8. V. Leung and F. Ko, *Polym. Adv. Technol.*, **2011**, *22*, 350–365.
9. A. Singh and N. Singh, *World J. Pharm. Res.*, **2017**, *6*, 611–631.
10. Y. Meng, G. Liu, A. Liu, Z. Guo, W. Sun and F. Shan, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 10805–10812.
11. C. Moldovan, R. Iosub and A. Manolescu, *Rev. Roum. Chim.*, **2012**, *57*, 559–567.
12. C. Dhand, N. Dwivedi, J. Loh and N. Jie, *RSC Adv.*, **2015**, *5*, 105003–105037.
13. J. H. Kim, *Appl. Surf. Sci.*, **2017**, *423*, 641–674.
14. A. Veerabhadraiah, S. Ramakrishna and G. Angadi, *Appl. Nanosci.*, **2017**, *7*, 355–363.
15. M. Elkasaby, H. A. Hegab, A. Mohany and G. M. Rizvi, *Adv. Polym. Technol.*, **2017**, 1–9.
16. I. M. Szilágyi, E. Santala, M. Kemell, T. Nikitin, L. Khriachtchev, M. Räsänen and M. Ritala, *J. Therm. Anal. Calorim.*, **2011**, *105*, 73–81.
17. I. M. Szilágyi and D. Nagy, *J. Phys. Conf. Ser.*, **2014**, *559*, 12010.
18. S. M. George, *Chem. Rev.*, **2010**, *110*, 111–31.
19. H. Kim, H. Lee and W. J. Maeng, *Thin Solid Films*, **2009**, *517*, 2563–2580.
20. S. I. Boyadjiev, O. Kéri, P. Bárdos, T. Firkala, F. Gáber, Z. K. Nagy, Z. Baji, M. Takács and I. M. Szilágyi, *Appl. Surf. Sci.*, **2017**, *424*, 190–197.
21. I. M. Szilágyi, E. Santala, M. Heikkilä, V. Pore, M. Kemell, T. Nikitin, G. Teucher, T. Firkala, L. Khriachtchev, M. Räsänen, M. Ritala and M. Leskelä, *Chem. Vap. Depos.*, **2013**, *19*, 149–155.
22. C. L. Beyler and M. M. Hirschler, *SFPE Handb.*, 110–131.
23. S. K. Shakshooki, A. A. Elejmi, A. M. Hamassi and N. A. Masoud, *Phys. Mater. Chem.*, **2014**, *2*, 1–6.
24. L. C. Mendes, R. C. Rodrigues and E. P. Silva, *J. Therm. Anal. Calorim.*, **2010**, *101*, 899–905.
25. Z. Jovanovic, A. Radosavljevic, M. Siljegovic, N. Bibic, V. Miskovic-Stankovic and Z. Kacarevic-Popovic, *Radiat. Phys. Chem.*, **2012**, *81*, 1720–1728.
26. N. S. Alghunaim, *Results Phys.*, **2016**, *6*, 456–460.