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ORIGINAL PAPER

Electrospun composite fibers of polyvinylpyrrolidone with embedded poly(methyl methacrylate)–polyethyleneimine core–shell particles

**Thammasit Vongsetskul · Phornpimon Kongjumnean ·
Panya Sunintaboon · Ratthapol Rangkupan ·
Pramuan Tangboriboonrat**

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Abstract Composite fibers consisting of poly(methyl methacrylate)–polyethyleneimine (PMMA–PEI) core–shell particles embedded in polyvinylpyrrolidone (PVP) were successfully fabricated by the electrospinning method. The electrospun fibers were produced using 18 % w/v aqueous PVP solution blended with 2 % w/v PMMA–PEI particles at various pH (1, 2, 3, and 4) with a fiber collection distance set at 10 cm. The applied electrical voltages (10, 12, 14, and 16 kV) significantly affected the morphology and diameter of the prepared composite fibers (141–353 nm). The smallest composite fibers were obtained from the spinning mixture at pH 2 and a voltage of 14 kV. The composite fibers would potentially be applied as drug and bioactive compound carriers.

Keywords Electrospinning · Composite fiber · Core–shell particle · Polyvinylpyrrolidone · Polyethyleneimine

Introduction

Electrospinning is one of the simplest methods for fabricating ultra-fine fiber from either polymer solution or polymer melt. In this process, a continuous strand of a

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T. Vongsetskul (✉) · P. Kongjumnean · P. Sunintaboon · P. Tangboriboonrat
Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Phyathai,
Bangkok 10400, Thailand
e-mail: thammasit.von@mahidol.ac.th

R. Rangkupan
Metallurgy and Materials Science Research Institute, Chulalongkorn University, Phyathai Road,
Pathumwan, Bangkok 10330, Thailand

R. Rangkupan
Center of Innovative Nanotechnology, Chulalongkorn University, Phyathai Road, Pathumwan,
Bangkok 10330, Thailand

polymer fluid is drawn through a spinneret by a high-electrostatic force. The obtained fibers are randomly deposited onto a grounded collector as a non-woven mat. The interesting characteristics of ultra-fine fiber are high-surface area to mass or volume ratio with high-porous mat. Since their surface is easy to be functionalized, ultra-fine fibers are suited for a wide variety of applications such as bioengineering, biotechnology, energy, electronics, environmental engineering, and security [1]. Recently, ultra-fine fibers have been applied for the inclusion of bioactive constituents for pharmaceutical applications [2]. The advantages of this technique are repeatability and controllability of nanofiber dimension [2, 3].

Among various types of electrospun fiber [1], the particle/polymer composite ultra-fine fiber is of great interest due to the combined properties of both ultra-fine fiber and the filler itself. The embedment of the fillers or nanoparticles into polymer fibers via the electrospinning technique is one of the approaches to avoid the risk of the penetration of nanoparticles into human body.

In the electrospun polyvinylpyrrolidone (PVP)/AgCl nanoparticles composite ultra-fine fibers prepared via the reaction of silver ions and HCl, it was found that most of AgCl nanoparticles were uniformly dispersed in the PVP fibers [4]. Later, the electrospun PVP/AgBr nanoparticles composite ultra-fine fibers were fabricated from PVP, $AgNO_3$, and bromide ion precursors via the sol–gel technique [5]. The existence of the AgBr nanoparticles was confirmed by X-ray photoelectron spectroscopy (XPS) and X-ray diffractometer (XRD) patterns.

For the monodisperse particles of conducting polypyrrole (PPy), synthesized directly by the emulsion polymerization in the presence of $FeCl_3$ and PVP in organic solvents, [6] results showed that the particles were almost in spherical form capped with PVP. The particle size ranged from 30 to 60 nm with a narrow size distribution when molecular weight (MW) of PVP was 3700 k and decreased from 90–110 to 60–80 nm with increasing in MW of PVP from 40 to 3600 k. The PPy particles were easily dispersed in solvents such as water, methanol, butanol, and isopropanol, and the dispersion could be blended with organic polymeric binders for film formation.

It is well known that the core–shell morphology allows the protection of the encapsulated substances inside the shell and controlling the release of the active ingredients. Therefore, the combination of core–shell particles and fibers could bring materials with unique morphology and multi-functions intrinsically from both components. Even though the composite fibers could give very unique-classed materials and is very challenging, there is no report on the preparation of core–shell polymer particle composite ultra-fine fibers. In 2010, both electrospun polyimide (PI) and Fe-FeO nanoparticles reinforced PI nanocomposite fibers were successfully prepared [7]. It was found that the morphology of the obtained fibers was correlated to the rheological properties of the PI and Fe-FeO/PI nanocomposite spinning mixtures. The thermal stability of the nanocomposite fibers was improved after the embedment. The glass transition temperature and melting temperature of the fibers increased by 10–12 and 15–17 °C, respectively. The magnetic properties of the Fe-FeO nanoparticles in the fibers differed from those of the as-received nanoparticles. For example, the saturation magnetizations (M_s) of as-received particles and those in fibers were 108.1 and 30.6 emu/g, respectively. Also, the coercivity increased from 62.3 Oe for as-received particles to 188.2 Oe for the particles dispersed in the fibers, which indicated that the particles became magnetically harder after being dispersed in the PI matrix within the composite fibers.

In 2012, the study on the preparation of polymer ellipsoids by the electrospinning of swollen nanoparticles was reported [8]. First, the nanoparticles were dispersed and swollen in the spinning mixtures before being electrospun. Then, the nanoparticles embedded in electrospun fibers were recovered by removing the fiber matrix. It was found that the electrospinning technique, a continuous process, could deform spherical into ellipsoidal nanoparticles successfully.

In this study, the poly(methyl methacrylate)–polyethyleneimine (PMMA–PEI) core–shell particles whose potential applications involved drug delivery [9] and antibacterial agent [10] were embedded by the electrospinning process in PVP, a biocompatible polymer [11]. The aim was to fabricate the composite ultrafine fibers as a new material which would potentially be applied as drug and bioactive compound carriers. The effects of the applied electrical voltages and pH of the spinning mixtures on the prepared fibers were studied inclusively.

Experimental

Materials

Polyvinylpyrrolidone ($\geq$95 %) with MW of 1.3×10^6 g/mol and PEI (50 % w/v in H_2O) with MW of 7.5×10^5 g/mol were purchased from Sigma-Aldrich (United States) and used without further purification. Deionized water (DI, 2A grade) was used to prepare the electrospinning mixtures and to dilute PEI to 10 wt%. Methyl methacrylate (MMA, 99 %) and *t*-butyl hydroperoxide solution (TBHP, 70 wt% in water) were purchased from Fluka. TBHP was used as received, whereas MMA was purified by passing through a column packed with alumina adsorbents. 1.0 M hydrochloric acid (HCl) was added into the electrospinning mixtures to adjust the pH.

Preparation and characterization of PMMA–PEI latex

Poly(methyl methacrylate)–polyethyleneimine core–shell latex particles were prepared by the emulsifier-free emulsion polymerization with an amine/TBHP initiating system [10]. The synthetic procedure was briefly described as follows: the polymerization was conducted in a 100-mL water-jacketed glass reactor equipped with a reflux condenser, nitrogen inlet, thermostat water bath, and magnetic stirrer. A total weight of 50 g was generally used. The PEI aqueous solution (10 % w/v, pH 7) was purged with nitrogen gas for 30 min. Water was pumped through the jacketed reactor from a thermostat water bath, which was controlled at 80 ± 1 °C. The MMA monomer (1 g) was charged to the reactor, followed by an addition of TBHP aqueous solution (1 g, 5 mM) to initiate polymerization. Then, the polymerization was continued for 2 h in a nitrogen environment.

The obtained particles were purified by an ultra centrifuge (L-XP Series Class R, Beckman, USA) at 30,000 rpm for 30 min. The zeta potential of particles was measured by an electrophoretic light scattering (ELS), using Zetasizer (Nano ZS, Malvern, UK) in 1 mM NaCl solution at room temperature.

Preparation and characterization of the spinning mixture

Polyvinylpyrrolidone dissolved in DI water was mixed with the PMMA–PEI latex to obtain the final PVP concentration of 18 wt% and the core–shell particle concentration of 2 wt%. Then, the mixtures were left under magnetic stirring for 30 min and their pH were measured (pH meter; model 215, Denver Instrument, USA). The viscosity and the conductivity of the spinning mixture were determined by a parallel rheometer (MCR 500, Anton Parr, Germany) at 25 °C and with a conductivity meter (Orion 105, Orion Research, USA), respectively.

Fabrication of PMMA–PEI/PVP composite fiber mat

Each of the spinning solution was loaded into a plastic syringe using a blunt 18-G stainless-steel needle (OD = 0.91 mm) as a nozzle. A Gamma High-Voltage Research ORMOND BEACH power supply (D-ES50PN-20w/QAM, FL, USA) was used to charge the spinning solution by connecting the emitting electrode of positive polarity to the nozzle. The distance between the tip of the nozzle and the collection device was 10 cm. Both the applied electrical voltages (10, 12, 14, and 16 kV) and pH (1, 2, 3, and 4) of the spinning mixture were varied in order to investigate their effect on the morphological appearance of the obtained composite fibers. The feed rate of the solutions was controlled at ~ 1.5 ml h^{-1}. Electrospinning was carried out in room conditions (i.e., 25 ± 1 °C; 71 ± 3 % of relative humidity). The collection time was fixed at 30 min.

Characterization of PMMA–PEI/PVP composite fiber mat

The morphology of the electrospun composite fibers was investigated under scanning electron microscope (SEM; S-2500, Hitachi, Japan) and transmission electron microscope (TEM; JEM-1400, JEOL, Japan) at 100 kV. The fibers were dried on an aluminum foil in a dust-free environment before being stuck on the sample holder with a double-coated carbon conductive tape and sputter-coated (E-102, Hitachi, Japan) under vacuum. An average diameter of the electrospun fiber mats was measured directly from SEM (at 15 kV) using a Photoshop 5.0 ($n \geq 50$). ATR-FTIR spectrophotometer (Equinox 55, Bruker, Germany) with a PIKE MIRacle$^{\mathrm{TM}}$ ATR accessory equipped with a single reflection ZnSe crystal was employed to characterize the functional groups and to confirm of the presence of core–shell particles on the composite fibers.

Results and discussion

Effect of pH of the spinning mixture

SEM images of the composite fibers prepared from the spinning mixtures with pH of 1, 2, 3, and 4 at 14 kV are shown in Fig. 1.

It was observed that the surface of the obtained composite fibers were smooth. From the SEM micrographs, the diameters of ultra-fine fibers were 200 ± 12, 141 ± 10, 260 ± 15, and 277 ± 15 nm when the pH of the spinning mixtures varied from 1, 2, 3, to 4, respectively. It was observed that the thinnest uniform composite fibers were obtained when the pH of the spinning mixtures was 2. To explain these results, the electrical conductivity and the viscosity of the spinning mixtures at different pHs were considered, and the data are presented in Figs. 2 and 3, respectively.

Figure 2 shows two main features. First, the electrical conductivity increased with decreasing pH. This could be attributed to the reduction of the pH value which indicated the increase in the concentration of hydronium ion, one of the conductive species. Second, the electrical conductivity of the core–shell particle/PVP mixtures was lower than that of the PVP solution at all pHs. It was believed that the presence of PEI could absorb the hydronium ions from the spinning mixtures as a result of protonation, in the shell of particles. This explanation was supported by the zeta-potentials of PMMA–PEI particles of 25.0 ± 4.7, 29.9 ± 0.8, 41.6 ± 1.7, and 40.0 ± 0.6 when the pH was 1, 2, 3, and 4, respectively. Since the electrostatic and Coulombic repulsion forces are vital in the formation of electrospun ultra-fine fibers, the electrospun fibers prepared from highly conductive spinning mixtures were generally thin. However, the very high-electrical conductance of the spinning mixtures could result in the fast travel of polymer from spinneret to fiber collector. Consequently, a flight time is too low to allow Coulombic repulsion to fully stretch and elongate the polymer jet. Thus, the diameter of the composite fibers slightly increased when the pH decreased from 2 to 1.

The viscosity of the spinning mixtures was also used to explain the effect of pH on the morphology of composite fibers as shown in Fig. 3.

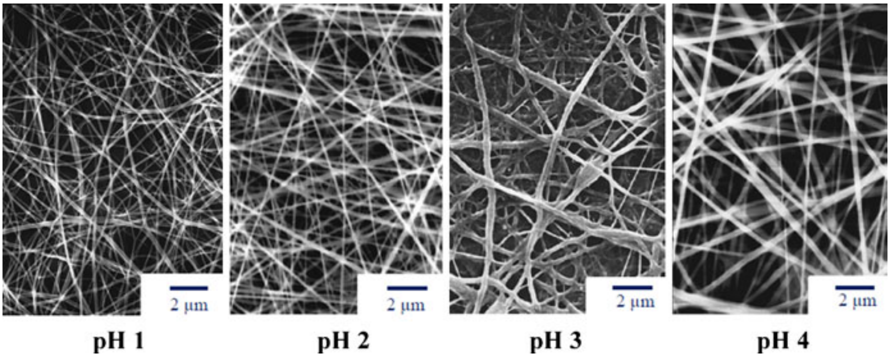

Fig. 1 SEM images of the composite fibers fabricated from 14 kV at various pH

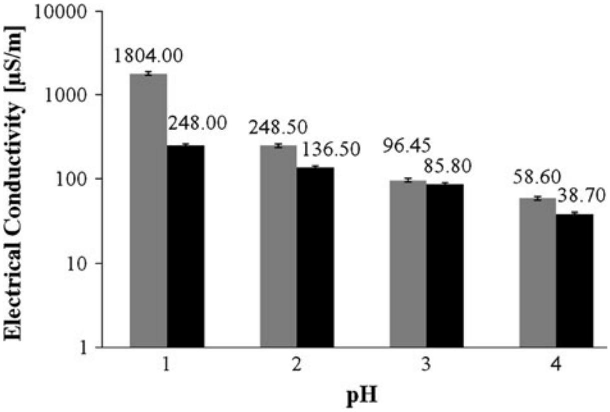

Fig. 2 Relationship between the electrical conductivity without and with core–shell particles (*gray* and *black*, respectively) and pH of the spinning mixtures

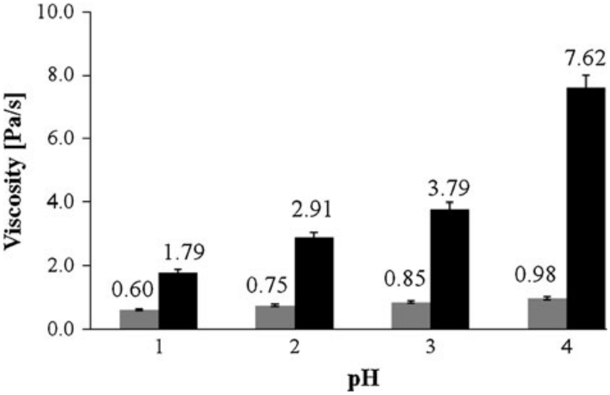

Fig. 3 Viscosity of PVP solutions (*gray*) and of the spinning mixtures (*black*) versus pH of the spinning mixtures

The viscosity of the core–shell particles/PVP mixture was higher than that of the PVP solution possibly due to the interaction and entanglement between PEI from the shell of the particles and PVP chains via the hydrogen bonding. In addition, the viscosity of the spinning mixture decreased with increasing the hydronium ion concentration (or decreasing pH). Since the amine groups of PEI shell were positively charged, they could not form the hydrogen bond with PVP. With less chain entanglement between PVP and PEI chains, the viscosity of the spinning mixtures was lower and it was more convenient for both electrostatic force and Coulombic repulsion to pull the polymer strand to form thin electrospun composite fibers.

Effect of applied electrical voltage

The average diameters of the composite fibers as a function of the applied electrical voltages and pH of the spinning mixtures are shown in Fig. 4.

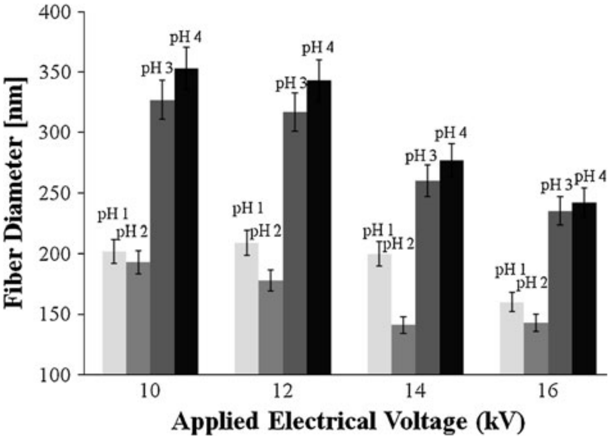

Fig. 4 Relationship between the fiber diameters and the applied electrical potentials at pH of the spinning mixtures (pH 1 = the *light gray* bar, pH 2 = the *gray* bar, pH 3 = the *dark gray* bar, and pH 4 = the *black* bar)

The diameter of the composite fibers decreased with increasing the applied electrical voltages. This was because the higher voltage led to the greater amount of charges, which accelerated the jet velocity and, hence, the stretching of the fibers [1]. Moreover, a high voltage favored the formation of secondary jet, which is the jet erupting from the jet coming from the spinnerette directly, during electrospinning which also contributed the reduction in the fiber diameter [12].

At pH 2, the diameter of the composite fibers decreased with increasing the applied voltages from 10 to 14 kV and did not decrease further when increasing from 14 to 16 kV. The insignificant change in diameter was probably because PVP chains were fully stretched. It was, therefore, assumed that the optimal conditions for fabricating the thinnest PMMA–PEI/PVP composite fibers were pH 2 and 14 kV.

Morphology of PMMA–PEI/PVP composite fibers

In order to confirm the presence of the core–shell particles in the composite fibers prepared from using the optimal conditions, these fibers were subjected to ATR-FTIR and TEM. The ATR-FTIR spectra of PVP, PMMA–PEI core–shell particles, and the composite fibers are displayed in Fig. 5.

ATR-FTIR spectrum of PVP (a) shows a strong band at 1665 cm^{-1} relating to N–H bending mode. In the spectrum of the core–shell particles (b), a characteristic peak at 1730 cm^{-1} corresponding to C=O stretching was observed [10]. The spectrum of the composite fibers (c) consisting of the signals from PVP and the core–shell particles confirmed that the fibers composed of both components. The morphology of the composite fibers under TEM is shown in Fig. 6.

The dark area in the TEM images was identified as the core–shell particles, whose size ranged from 100 to 150 nm, embedded in the PVP ultra-fine fibers. The

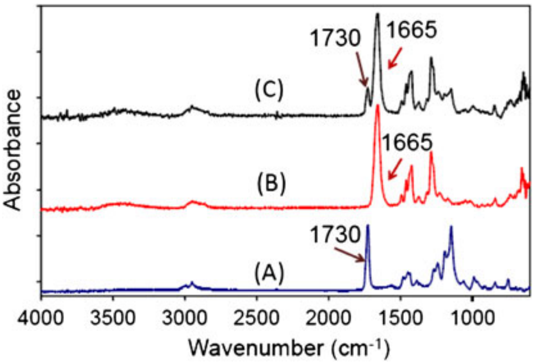

Fig. 5 ATR-FTIR spectra of **a** PMMA–PEI core–shell particles, **b** PVP, and **c** the electrospun PMMA–PEI/PVP composite fibers

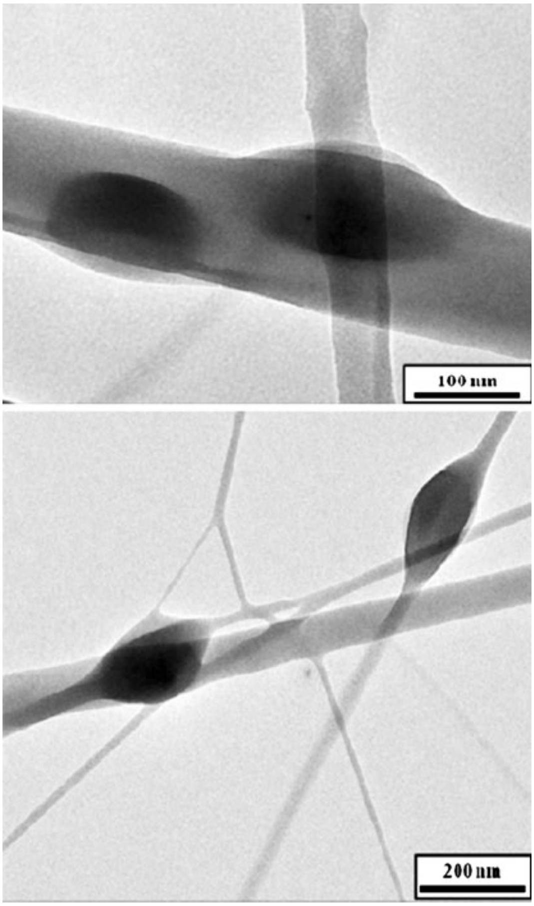

Fig. 6 TEM images of PMMA–PEI/PVP composite fibers prepared from applying 14 kV and pH 2

shape of PMMA–PEI particles was distorted from spherical to ellipsoidal because of the electrostatic force and Coulombic repulsion acting on the polymer strand during the fiber fabrication process. It was observed that the fibers with diameter of 239 nm are large enough to embed the core–shell particles. The morphology was in accordance with the FTIR spectra which confirmed that PMMA–PEI core–shell particles were successfully incorporated into the composite fibers.

Conclusion

SEM images, TEM micrographs, and ATR-FTIR spectra confirmed the success of the preparation of PMMA–PEI/PVP composite fibers with diameter of 141–353 nm by the electrospinning technique. The optimal conditions providing the smallest and uniform composite fibers were at pH 2 and 14 kV. The composite fibers of PMMA–PEI core–shell polymer particles and PVP biocompatible polymer were successfully prepared and would be potentially used in biomedical applications such as drug delivery systems.

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References

1. Ramakrishna S, Fujihara K, Teo W, Lim T, Ma Z (2005) An introduction to electrospinning and nanofibers. World Scientific Publishing, Singapore
2. Kontogiannopoulos KN, Assimopoulou AN, Tsivintzelis I, Panayiotou C, Papageorgiou VP (2011) Electrospun fiber mats containing shikonin and derivatives with potential biomedical applications. Int J Pharm 409(1–2):216–228. doi:10.1016/j.ijpharm.2011.02.004
3. Fletcher BL, McKnight TE, Fowlkes JD, Allison DP, Simpson ML, Doktycz MJ (2007) Controlling the dimensions of carbon nanofiber structures through the electropolymerization of pyrrole. Synth Met 157(6–7):282–289. doi:10.1016/j.synthmet.2007.03.004
4. Bai J, Li Y, Li M, Wang S, Zhang C, Yang Q (2008) Electrospinning method for the preparation of silver chloride nanoparticles in PVP nanofiber. Appl Surf Sci 254:4520–4523. doi:10.1016/j.apsusc.2008.01.051
5. Bai J, Li Y, Zhang C, Liang X, Yang Q (2008) Preparing AgBr nanoparticles in poly(vinyl pyrrolidone) (PVP) nanofibers. Colloids Surf A 329:165–168. doi:10.1016/j.colsurfa.2008.07.010
6. Woo H, Jung W, Ihm D, Kim J (2010) Synthesis and dispersion of polypyrrole nanoparticles in polyvinylpyrrolidone emulsion. Synth Met 160:588–591. doi:10.1016/j.synthmet.2009.12.010
7. Zhu JH, Wei SY, Chen XL, Karki AB, Rutman D, Young DP, Guo ZH (2010) Electrospun polyimide nanocomposite fibers reinforced with core-shell Fe-FeO nanoparticles. J Phys Chem C 114:8844–8850. doi:10.1021/jp1020033
8. Herrmann C, Turshatov A, Crespy D (2012) Fabrication of polymer ellipsoids by the electrospinning of swollen nanoparticles. ACS Macro Lett 1:907–909. doi:10.1021/mz300245b
9. Pimpha N, Chaleawlert-umpon S, Sunintaboon P (2012) Core/shell polymethyl methacrylate/polyethyleneimine particles incorporating large amounts of iron oxide nanoparticles prepared by emulsifier-free emulsion polymerization. Polymer 53(10):2015–2022. doi:10.1016/j.polymer.2012.03.019
10. Inphonlek S, Pimpha N, Sunintaboon P (2010) Synthesis of poly(methyl methacrylate) core/chitosan-mixed-polyethyleneimine shell nanoparticles and their antibacterial property. Colloids Surf B 77(2):219–226. doi:10.1016/j.colsurfb.2010.01.029
11. Fischer F, Bauer S (2009) Polyvinylpyrrolidon. Ein Tausendsassa. Chem Unserer Zeit 43(6):376–383. doi:10.1002/ciuz.200900492
12. Demir MM, Yilgor I, Yilgor E, Eman B (2002) Electrospinning of polyurethane fibers. Polymer 43:3303–3309. doi:10.1016/S0032-3861(02)00136-2