

Sustainable Bioplastics 2016 - Electrospun fibers from biosourced and biodegradable polymers for biotechnological applications

Jean-François GERARD

European Polymer Federation, France

Electrospinning process is one of the most promising routes for the design and development of smart textiles based on polymer nanofibers. From a proper selection of the electrospinning process parameters and polymers, (multi)functional textiles could be proposed. In this lecture, we will show how biobased polymers, such as PLA-based, and biodegradable polymers, such as PBAT, can be used to prepare electrospun scaffolds. In the first part, electrospinning is applied to neat polylactic acid (PLA) and to PLA-based blends, i.e. PLA/polyethylene glycol-b-polylactic acid block copolymers and PLA/PEG homopolymer. Electrospun membranes exhibit fibers having diameters from 110 to 310 nm depending on the composition and large amounts of porosity (about 80% vol.) which are required for cell culture application. In vitro degradation, as well as the hydrophilicity of the electrospun scaffolds, can be finely tuned from material composition. Fluorescence microscopy shows that the PLA electrospun fibers based scaffolds are good candidates for the survival and proliferation of neural stem cells. Even if the introduction of hydrophilic segments, i.e. polyethylene glycol from PLA-b-PEG block copolymer, leads to the same level of proliferation than PLA-based membranes, the PLA/PLA-b-PEG electrospun membranes exhibited the suitable hydrolytic degradation required for implantable scaffolds. The second part deals with the development of biodegradable PBAT electrospun membranes with potential applications in the field of smart textiles. As mentioned previously, the fiber morphology is strongly dependent on the tip-collector distance, concentration, and applied voltage. Smooth fibers and beads free membranes could be prepared and analyzed to establish morphology-properties relationships. PBAT membranes having the best thermal and mechanical properties were selected as host of a curli protein which is able to complex heavy metals. In fact, by electrospinning, porous membranes exhibiting a large surface-to-volume ratio could be proposed for chelation of pollutants such as nickel.

Montmorillonite clays are widely used in catalytic processes. Cracking catalysts have used montmorillonite clays for more than 60 years. Other acid-based catalysts use acid-treated montmorillonite clays.

Similar to many other clays, montmorillonite swells with the addition of water. Montmorillonites are expanding considerably more than other clays because of water penetrating the interlayer molecular spaces and as a result the quantity of expansion is mainly due to the type of interchangeable cation in the sample. The presence of sodium because the clay swelling to its original volume may be repeatedly caused by the greatest interchangeable cation. Accordingly, sodium montmorillonite

was used because it is the most important ingredient in non-component agents for splitting rock in natural stone quarries in an attempt to limit the amount of waste, or to demolish concrete structures where it is impossible to use removal of explosive charges.

Because of this reconstructive property bentonite containing montmorillonite is also useful as a seal or annular additive for water wells and as a protective liner for landfills. Other uses include as an antidepressant agent in animal feed, in paper-making to reduce deposit formation, and as a maintenance and drainage assistance component. Montmorillonite was used in cosmetics.

In fine powder form, it can also be used as a flocculant in ponds. It is thrown to the surface because it falls into the water, making the water "cloudy", attracts small particles within the water and settles on the lower one, cleansing the water. Koi and goldfish (carpet) then feed the "clump" which helps digest the fish. It is sold in pond supply stores.

Sodium montmorillonite is also used due to the origin of some cat litter products, due to its adsorbent and clumping properties. Introduction A low Young's modulus and biocompatibility are two important criteria for biomedical applications. Stainless steel and Co-Cr alloys have widely been used as metallic biomaterials for orthopedics and implants thanks to their favorable mechanical properties and thermal stability. However, the Young's modulus of those alloys ($\approx 210\text{--}240$ GPa) is far above that of human bone ($\approx 10\text{--}30$ GPa). The high Young's modulus results in bone stress shielding, which is harmful to human health. Ti-Ni alloys have been extensively applied for biomedical uses to date, but it has been pointed out that pure Ni is toxic and can cause Ni-hypersensitivity. Over the past decade, efforts have been made to remove cytotoxic nickel elements from biomaterials and replace them with non-toxic and allergy-free biocompatible elements. β -type titanium alloys have attracted attention for biomedical applications due to their low stiffness, good corrosion resistance, biocompatibility, and superelasticity. The β -type Ti-based alloys exhibit two stable phases, the β phase (bcc) and the α phase (hcp), along with exhibiting a number of metastable phases including α_0 (hexagonal), α' (orthorhombic), and ω phases. The volume fraction of the β phase are often enhanced in titanium alloys by β -stabilizing transition metal (TM) elements like Mo, V, Nb, Cr, Zr, and Ta. Tantalum and niobium are considered the most potent β stabilizers and effectively reduce the modulus of elasticity of titanium alloys. On its own, zirconium is taken into account a neutral and weak β stabilizer. However, this element begins to act as a more potent β stabilizer by playing a role in binding to Nb. These alloys are much

costlier than pure titanium and Ti-6Al-V, due to the addition of pricy Nb and Ta. In addition, large amounts of heavy elements, like Nb, Mo, and Ta, lead to considerable increases within the density of β -type titanium alloys. Therefore, research and development of titanium alloys that are low cost, have a low Young's modulus, and are light-weight are of high importance for biomedical applications. The Ti-Nb-Zr alloy system has proved to be an honest substitute for developing absolutely safe Ni-free biomedical Ti alloys. Ti, Nb, and Zr are non-toxic elements and thus don't cause any adverse reaction within the physical body. The addition of Zr to the β -type Ti-Nb alloy is beneficial for increasing the superelasticity, enhancing corrosion resistance, the utmost recovered strain, and thus the critical stress for slip deformation compared with Ta, and thus shows promising potential for biomedical applications. An alternative to obtaining the desired smaller elastic modulus is to engineer porous structures, such as mimicking those in bones.

Biography:

Prof. Jean-François GERARD got his PhD diploma in Polymer Science in 1985 from researches dedicated to syntheses of zwitterionic polyurethanes from sulfo-betainic diols for self-emulsifying systems. He joined in 1986 CNRS as permanent scientist and his expertise deals with interfaces in polymer-based materials and nanostructured polymers. He is author of about 240 papers in international journals and 110 invited lectures in international conferences. He acts also as vice-president of the European Center for Nanostructured Polymers) and President of the European Polymer Federation.

References:

1. Ziabicki, A. (1976) Fundamentals of fiber formation, John Wiley and Sons, London, ISBN 0-471-98220-2.
2. High speed video of the taylor cone formation and electrospinning. youtube.com
3. Single nozzle electrospinning process nanofiber formation video. youtube.com
4. High speed video of the whipping instability. youtube.com
5. Li, D.; Xia, Y. (2004). "Electrospinning of Nanofibers: Reinventing the Wheel?". *Advanced Materials*.
6. Merritt, Sonia R.; Agata A. Exner; Zhenghong Lee; Horst A. von Recum (May 2012). "Electrospinning and Imaging". *Advanced Engineering Materials*.
7. Varesano, A.; Carletto, R.A.; Mazzuchetti, G. (2009). "Experimental investigations on the multi-jet electrospinning process". *Journal of Materials Processing Technology*. 209 (11): 5178–5185.
8. Liu, Y.; He, J.-H.; Yu, J.-Y. (2008). "Bubble-electrospinning: a novel method for making nanofibers". *Journal of Physics: Conference Series*. 96 (1): 012001. Bibcode:2008JPhCS..96a2001L.
9. Nagy, Z.K.; Balogh, A.; Démuth, B.; Pataki, H.; Vigh, T.; Szabó, B.; Molnár, K.; Schmidt, B.T.; Horák, P.; Marosi, G. (2015). "High speed electrospinning for scaled-up production of amorphous solid dispersion of itraconazole" (PDF). *International Journal of Pharmaceutics*.