SILVER PARTICLES INCORPORATION TO NANOFIBRE STRUCTURE FOR SURFACE MEMBRANE MODIFICATION

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Abstract

Current research is focused on the surface membrane modification of existing industrially produced ultrafiltration membranes with different types of polymeric nanofibres, for the purpose of added functionality (e.g., catalysts, biodegradable particles and substances). In our case we focused on biocide (antimicrobial) surface properties using silver dispersion or silver precursors. Research is aimed to find the optimal conditions of electrospinning process as well as maximum of concentration and required kinetics of silver particles releasing and for the preparation of composite ultrafiltration membrane with surface nanofibre layer with biocide properties.

Keywords: Nanofibres, electrospinning, silver dispersion, silver precursors, ultrafiltration membrane.

1. PREPARATION OF VARIOUS POLYMERIC NANOFIBRES WITH SILVER

Nanofibers are prepared using the method called electrospinning, when fibres are formed by the effect of electrostatic field from a thin layer of a polymer solution. The capability of a polymer to form fibers is affected by a number of process and system parameters such as the intensity of electric field, viscosity, molar mass, surface tension, polymer concentration, etc.

From the point of view of incorporation of special additives in the form of suspension into nanofibers is necessary to modify/ increase a viscosity of polymer solution and this additives affects the properties and homogeneity of spinning solution. A portion of particles which still enables electrospinning is therefore limited.

1.1 Preparation of polyurethane with silver

Firstly Polyurethane (PUR) based on 30% standard solution (Laritan) in Dimethylfomamid (DMF)/additives solvent system was used. Nanofibre layer shows hydrophobic behaviour, which could be significant for membrane fouling. Advantageous is chemical and mechanical stability and dissolubility in water.

1.1.1 Disperse addition

Silver nanoparticles in aqueous disperse (provided by University in Olomouc) was used for the experiment. Mean size of particles 15 nm, the concentration of 3000 mg/l, with Polyacrylate surface stabilizer. Limiting factor is aqueous disperse phase, which limits the total silver amount.

Compare to pure Polyurethane solution, silver addition negatively affects the homogeneity and fibre structure, resulting in wider fibre diameter. For hand-spinning plasma effect was observed and inhomogeneous fibre release on surface of the solution. The flow of plasma could be caused by loss of valence in strong electric field. The effect however, could be explained by ionization of air molecules in high intensity electric filed.

Surface charge of silver particles can also have a major impact to limited mobility of the partially charged polar groups of the polymer in electric field. Absolute concentration of silver in nanofibre product was determined at 4.8 mg/m². Absolute solution concentration of Ag in Polyurethane was about 0.003 (wt/wt). Nanofibres were collected on Polypropylene (PP) spunbond (Pegas Nonwovens).
Calibration of the initial size of particles in the dispersion (15 nm) was made on device ZetaSizer, working on scattering light principle and conforming the reported particle size in the dispersion. The mean size of aggregates was determined (using this method) to 350 nm.

Fig 1. Polyurethane fibres with dispersal silver

1.1.2 Silver precursors addition
Silver salts was dissoluted to the maximum degree of dissociation in water as a part of spinning solution. The nanofibres were prepared without tetraethylamoniumbromide (TEAB) addition. Relatively high concentrations of silver in polymer solution was achieved. Convinsious is the fact that Dimethylformamide is also reducting agent for ionic silver. Limitation is the total water addition amount to solvent system.

Properties Suppression of negative phenomena in the electrospinning compare to silver disperse additions was observed. It has got a positive impact on the structure and distribution of particles in the final sample. The difference between the resulting aggregates of ionic silver versus disperse silver could be explained by difference of surface charge and tendency to its minimization in strong electric field.

The mean size of salt particles in Polyurethane structure was evaluated to 200 nm (Zeta sizer) again with quite wide distribution of particle size. Absolute solution concentration of Ag in PUR was about 0.22 (wt/wt). Absolute concentration of silver for PUR was determined at 800 mg/m$^2$, which is many times over the amount than in case of a disperse silver. Kinetics of release, however, shows rapid exponential leaching of silver in the tens of hours, with the greatest loss occurs at the beginning of leaching in an aqueous environment. Total leaching concentration was up to 30mg/l for the sample with an area of 0.01 square meters. Analysis was made using luquid chromatography (HPLC) device.

1.2 Polyvinilalcohol nanofibres with silver
The advantage of the Polyvinylalcohol (PVA) nanofibres is its hydrophilic behaviour (suitable for UF membrane modifications) and a negligible risk to the environment due to aqueous solvent system. On the other hand nanofibres based on PVA are less chemical resistance than in the case of Polyurethane.

According to low molecular weight polyvinylalcohol (about 100kDa) needed for electrospinning, the nanofibre product is soluble in water. Therefore cross-linking agent is neccessary. For this purpose crosslinker based on dialdehyde was used with the initiation temperature of 150 °C for 80 min. The dialdehyde crossilinker compare to eg. formaldehyde has an increase in propability of networking the chains and degree of crosslinking. Despite networking the polymer the PVA fibres are partially swelling in aqueous environment and are brittle after drying.

1.2.1 Disperse addition
The same type of dipere as in case of Polyurethane was tested. Advantageous water based solvent system leads to higher silver concentration and more homogenous delivery than in previous case. The particles were smaller than in case of Polyuretane disperse (about 250 nm), however silver particles are far from demanded concentration and uniformity. Absolute concentration of silver in nanofibre product was determined at 15 mg/m$^2$. Absolute Concentration of silver in PVA was about 0.014 (wt/wt).
1.2.2 Silver precursors addition

Compare to disperse silver, also here the silver nitrate addition ensures much higher silver concentration in nanofibre structure and also in terms of homogenous delivery and electrospinning conditions the results are better. Here the limiting factor of total silver amount (differences from PUR) is electrospinning process itself. Absolute concentration of silver to PVA was about 0.128 (wt/wt). Smallest particle size bellow 100 nm (depending on silver and polymer initial concentration).

Fig 2. PVA nanofibres with silver (0.064 wt/wt)

1.2.3 Reduction methods

Advantages of zero-valent silver compared to ionic silver is smaller coagulation in environment with non-zero ionic strength. One way of subsequent reducing the silver ion form is by spraying ascorbic acid onto fibres surface. Use of Polyurethane is advantageous (partially reduced in solution with DMF) for high chemical resistance of 3% aqueous solution of ascorbic acid. PVA on the other hand has limited resistance in acidic pH. Hydrophobic/hydrophylic behaviour is also important for this procedure.

$$2 \text{Ag}^+ + \text{C}_6\text{H}_5\text{O}_6 \leftrightarrow 2 \text{Ag}^0 + \text{C}_6\text{H}_5\text{O}_6 + 2 \text{H}^+$$

Another possibility is reduction by UV light, because Ultra-violet light is well-known as reducting agent for metal ion particles. The advantage of this procedure is the avoidance of chemical stress to nanofibers. Disadvantage of this procedure is high exposure time.

Fig 3. PVA nanofibres with silver (0.128 wt/wt)

1.3 Polyethersulphone nanofibres

Finally Polyethersulphone (PES) nanofibres based on BASF Ultrason E6020P (Mw=51000, Mw/Mn=3.5) were used, which has good mechanical, thermal and hydroscopic properties and the great advantages is chemical compatibility with PES based industrial membranes. Based on the Hansen solubility parameters [2] different solvent were tested and functional substances were experimentally found with different nanofibre result.

1.3.1 Silver dispersal addition

The previous water-based disperse was tested. These tests were though not very promising in terms of homogeneity and total silver amount. Another disperse of 5% silver behenate in n-ethyl-2-pyrrrolidone (NEP) (provided by Agfa) was also tested. With linear formula AgC_{22}H_{46}O_{2} (Molecular Weight: 447.23, compare to 169.87 for silver nitrate), silver behenate belongs to long chain silver carboxylyte with low solubility. Organic phase is also suitable because Polyethersulphone tends to precipitin in water.

Properties During these test it turns out, that the addition of silver behenate dispersion leads to samples with promising fibre morphology and even to particles bellow fibre diameter. Maximum silver amount was estimated to 0.022 (wt/wt). There will be continuation of these tests.
1.3.2 Silver nitrate experiments

For silver nitrate various samples tested, as it can be seen from table 2. Various procedures of preparation lead to functional samples with different properties. Lower RH was also needed to achieve homogenous coverage of fibres. All these experiment were performed on hand spinning rod.

Properties

As seen from table 2 particles bellow fibre diameter were obtained (image measurement of particles (NIS Elements)). But still a few visible particles in full magnification range of used SEM devices. To obtain higher resolution images plating is needed. This makes the relatively high initial brightness of fibres even higher (plating by Ag) and the particles became apart few bigger clusters practically invisible.

To estimate the real particle size the post imaging software or TEM microscopy should be used. The discrepancy between visible particles and high initial silver concentration (up to 0.15 (wt/wt)), could be indicated from relatively smooth electrospinning process and depth colour of samples after exposure to daylight. For Polyethersulphone nanofibres with this type of silver addition, silver presence was confirmed using X-ray diffraction particle spectra method (at department of chemistry, TUL) with determination of other particles presence.

1.3.3 Silver benzoate and silver behenate tests

This both tested silver precursors are on the both side of silver carboxylates precursors row. With linear formula $C_6H_5CO_2Ag$ (molecular weight: 228.98), silver benzoate belongs to short chain carboxylates with higher solubility. Limitation of silver nitrate is higher solubility, and aggregation in strong electric field, limitation of silver behenate is low solubility. Silver benzoate could be somewhere between and therefore tested.

Properties For silver behenate the main limitation is low solubility that makes the solution non-homogenous and affects the nanofibres exposition significantly. Tested samples of silver benzoate on the other hand show good electrospining process, no visible aggregates and quite uniform fibres (few defects still present). Determination of silver particles size and uniformity will recently be made.
2. PREPARATION OF COMPOSITE MEMBRANE

The goal is the appropriate adhesion with minimal losses of nanofibre structure and membrane performances. Previous experiments were based on thermal-low pressure fixation of Polyurethane nanofibre layer on flat sheet experimental PES membranes (provided by Agfa, same BASF type) with and without meltblown Polyethylene/Polypropylene protection surface layer. During these tests, poor adhesion was achieved.

Actual experiments are on thermal-pressure fixation of nanofibres directly on flat sheet PES membranes. In the case of PVA and PUR nanofibres the structural losses were observed within temperatures below 140°C with significant cake-formation on membrane surface. PES nanofibres with higher temperature resistance are therefore preferable.

The appropriate adhesion that was achieved (together with acceptable nanofibre morphology), could be the result of lowering the $T_g$ (= 225 °C) of PES/additives and also result of residural solvent evaporation. Best results were for temperature interval 170-175 °C, with medium pressure. Higher pressure loads leads to structural changes of fibres.

Experiment has shown that the weaker spot of thermal-pressure lamination is adhesion between composite membrane layers and also the sensitivity of fibre layer. Appropriate adhesion and fibre morphology, together with membrane performance should be therefore further tested. For this purpose the experimental device is waiting to be built for real ultrafiltration simulations.

3. MEMBRANE ANTIMICROBIAL TESTING

Two standard methods of antimicrobial testing for bacterial kinds Escherichia coli – E.C. and Staphylococcus aureus S.A. were used.
1st method (AATCC 147) is a method that suggests a primary inhibitory effect of tested material. In this case it showed (thanks halo zones), the inhibitory effects of the of Polyurethane with dispersal Ag(0) and Polyurethane with silver nitrate.

2nd method (AATCC 100) exactly refers to the inhibitory effect of the tested sample. The best results were achieved in the sample Polyurethane with silver nitrate (SA - 100% inhibition and for EC -97.5% inhibition). In both cases it is an excellent antibacterial inhibitory effect.

Tested sample of Polyurethane with Ag(0) achieved also good inhibitory effect (for S.A. shows a 90.6% inhibitory effect on E.C. an 99.4%). In this case despite quite low silver content in nanofibre layers we can speak of very good and excellent (for EC) inhibitory effect. For further detail see [1].

4. CONCLUSIONS

It is in principle possible to get colloidal silver into nanofibre structure. Silver zero-valent subsidies lead to the changed conditions of electrospinning and to necessary intensification of the electric field. For existing spinning solutions, the fibres show a large deviation in size distribution of nanofibers as well as large and irregular units in their structure, indicating high aggregation instability of spinning solution in strong electric field. For the ionic form of silver it was observed suppression of described negative phenomena, which led to more uniform structure of the nanofibres and final size of silver particles in their structure. Also higher concentration of silver in the fibres structure was achieved. In contrast, in the non-reduced form the fast kinetics of particle oxidation was observed and thus loss of the required biocide properties of nanofibers. In this case subsequent chemical reduction of silver ions or using UV light is needed.

Polyetehsulphone nanofibres with silver nitrate, silver benzoate, and dispersion silver behenate shows promising results. Also in terms of composite membrane preparation this polymer type seems to be preferable. Pilot test shows that the preparation of composite membrane is achievable. Question remains the properties of real ultrafiltration conditions and a minimum loss of filtration membrane capability.

5. RESEARCH FOR NEXT PERIOD

- Improve fixation conditions to ensure adhesion and minimal/non morphology changes of fibres
- Testing membranes by real ultrafiltration condition
- Testing antimicrobial properties in long-term study

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