

Metallization of Poly(glycidylmethacrylate) Based Electrospun Nanofibers

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INTRODUCTION

Controlled metallization of polymer surfaces offers new possibilities for applications in the field of catalysis, flexible electronics, and filtration. Possibility of creating polymers with specific surface areas in excess of 200 m²/g intensifies their potential as substrates for electronics¹⁻², photonics³, medicine, sensors⁴, and catalyst industries⁵. It was shown that nanofibrous films have better performance in both sensitivity and time response compared to the continuous films^{6,7}. Electrospun mats composed of randomly distributed fibers with submicron diameters are a good candidate as a substrate material. The morphology of electrospun fibers, process parameters of fiber fabrication, and their properties were reported earlier in literature⁸. The presence of a uniform coating on template electrospun fibers facilitates the fabrication of metal or hybrid nano and meso tubes through the pyrolysis of the polymeric core⁹. A large number of metal deposition techniques, such as physical vapour deposition¹⁰, chemical vapour deposition¹¹, sputter deposition¹², have been employed to produce coatings for various substrates with a selection of shapes. An electroless plating technique which is based on metal deposition from its salt solution involves a room temperature process in an aqueous medium. In contrast to other deposition techniques (physical or chemical), this method proceeds through a redox reaction¹³. In one of the early works, a polymeric surface was first activated by reducing agents and then treated with the metal ion solution¹⁴. In the method presented in this work, the reducing agent hydrazine was immobilized on the nanofibers surface and the metal atoms were nucleated on the fibers in the aqueous solution of the metal ion. The polymer backbone possesses glycidyl methacrylate (GMA) and acrylonitrile (AN), in which former has functional groups that provide binding sites for the reducing agent on the pendant oxirane ring and later has good electrospinnability in DMF.

The metallization of polymeric nanofibers was recently reported by our group¹⁵. Palladium nanoparticles were produced by direct reduction of metal salt in the nanofibers. However, the coverage of Pd particles on the fibers was not enough to conduct electricity. In this work the aim was to generate a higher amount of metal particles on electrospun nanofibers to obtain a continuous path for electrical conduction. Electroless plating is especially suitable to silver plating since silver is a metal which facilitates autocatalytic reaction for its reduction¹³. Silver particles can be deposited evenly along the edges, inside cavities, and over irregularly shaped objects which are otherwise difficult to coat evenly. The combination of electrospinning and electroless plating was studied by Pinto and co-workers¹⁶. They electrospun inherently conductive polyaniline (doped with 2-acrylamido-2-methyl-1-propanesulfonic acid) in methylene chloride and coated nickel nanoparticles via electroless plating. Here we report a facile chemical route to obtain highly conductive nanofibers under ambient conditions using aqueous solution.

EXPERIMENTAL

PGMA and P(AN-GMA) were obtained by radical polymerization in dimethyl formamide (DMF) using 1 wt% ammonium persulphate initiator, carried out over a period of 24 h at 50°C. In P(AN-GMA) synthesis, amount of AN and GMA in the monomer mixture was 60 and 40 percent per mole, respectively. Copolymer composition was determined by using ¹H NMR. P(AN-GMA) was electrospun successively from solution in DMF under an electrical field. Spinning process had continued for nearly 6 hrs to obtain thick electrospun mat that was detached easily from the grounded foil. Electrospun polymer web was immersed into aqueous hydrazine in a 250-mL beaker and stirred overnight, than it was filtered and washed with an excess of distilled water that had been deoxygenized with a flow of nitrogen gas. The product

was dried at 50°C for 24 h in vacuum. The plating was performed soon after the surface modification. Hydrazine modified electrospun mat was introduced into a mixture of 5 ml of a 0.1 M AgNO₃ solution, 0.5 ml of a 1M KOH solution and 10 ml concentrated NH₃ solution in a closed glass bottle. Thermogravimetric Analysis (TGA) and Dynamic Thermal Analysis (DTA) were performed using Netzch STA449C under an oxidative media. Heating rate was 20 °C per minute starting from 27 °C up to 1000°C.

RESULTS AND DISCUSSION

PGMA and P(AN-GMA) solutions having 30 and 45 %wt of concentrations were subjected to 1.53 kV/cm electrical field and nanofibers with an average diameter of 1000 ± 100 and 170±50 nm were obtained, respectively. A two-step procedure was followed during the preparation of metal-coated polymer nanofibers as illustrated in Figure 1.

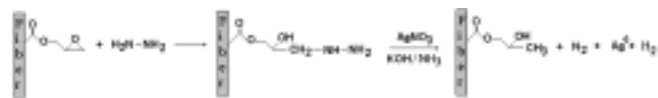


Figure 1. Surface modification and metallization reactions of PGMA and P(AN-GMA) nanofibers.

In the first step, we have attempted to replace the oxirane ring with a reducing agent. Hydrazine molecule, electron donor, was attached to polymer fiber surface through the opening of highly strained three member ring of glycidylmethacrylate. Hydrazination of oxirane ring was monitored by IR spectroscopy through disappearing bands of asymmetric stretching of oxirane group at 1129 cm⁻¹ and appearances of 3216 cm⁻¹ bands stemming from symmetric stretching of the -NH₂ (primary amine) group¹⁷. The hydrazination has no noticeable effect on the morphology of the fibers as observed by SEM. The second step was a redox reaction between hydrazine attached electrospun fibers and Ag cations in solution. Surface-modified electrospun nanofibers were allowed to react with an ammoniac solution of silver nitrate. A redox reaction took place during which metallic silver was nucleated along the fiber surface silver nanoparticles on the fibers 30-60 nm were in diameter. Oxidation of hydrazine reduces and deposits silver atoms on fibers surface under aqueous alkaline media. The deposited Ag particles were identified by X-ray diffraction (XRD) and imaged by using scanning and transmission electron microscopes. Figure 2 illustrates the XRD plot for P(AN-GMA) after the metallization process.

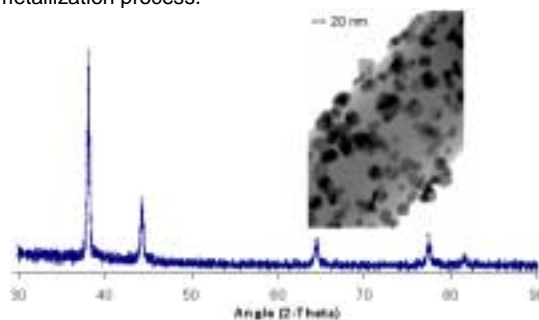


Figure 2. XRD of Ag particles on the P(AN-GMA) nanofibers. On the inset, Ag particles obtained from 1 minute deposition time in plating solution.

Four peaks were detected on the X-ray spectra between 30–90°. Main peak appeared around 2 θ = 38.1° corresponding to the (111) peak of Ag. The dimensions of the Ag particles were estimated by using Debye-Scherrer formula ($\beta = 0.9 \times \lambda / (\text{FWHM} \times \cos \theta)$)¹⁸. β is the size of the Ag crystals; FWHM is the value of full width at half maximum of the main peak. Particle diameters calculated from peak broadening of X-ray spectra matches with the diameters measured from the electron microscope images [Fig 2 (inset)]. This comparison indicates that silver atoms are mostly single crystals.

To confirm the level of metal on the electrospun mat, P(AN-GMA) mat and its metallized form were heated in oxidative media to remove the polymer. Thermo analytical curves of P(AN-GMA) and Ag coated P(AN-GMA) are presented in Figure 3. The thermo-oxidative decomposition of two products follows different paths

from room temperature to 1000°C. Degradation occurs and mass decreases as the temperature increases. While only 2% of polymer moiety remains beyond 770°C under the thermoxidative environment for electrospun mat of P(AN-GMA), 35% of the total mass was measured at the end of the thermal analysis for a metal deposited sample. The difference in the remnant mass of the samples before and after the metallization procedure was attributed to the amount of Ag deposited on the electrospun mat. The melting point of Ag, which was 961°C, is observed as an endothermic peak. The mass percentage of the metallized electrospun mat consists of both the metal particles produced on the nanofibers and the particles formed between the nanofibers. These particles agglomerate between fibers were unintentional and are to be minimized. Ultrasonication of the mat in aqueous media removed such agglomerates between nanofibers.

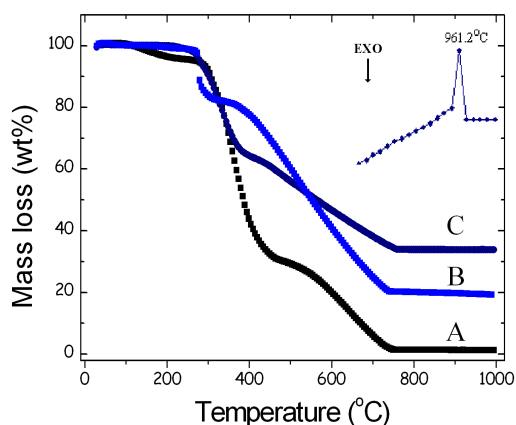


Figure 3. Thermo analytical curves of **A-** P(AN-GMA) electrospun mats, **B-** 10 minute Ag coated PAN mats, and **C-** 10 minute Ag coated P(AN-GMA) mats.

The electron microscope images of the samples before and after the sonication show that the particles remain on the nanofibers surface even after a 5 min sonication process. The TGA analysis of the sonicated sample gave the correct weight percentage of silver particles loaded onto the electrospun mat. The durability of the particles was also tested by keeping the metallized nanofibers in DMF, which is the solvent of the polymer. The mat does not dissolve, swells in DMF indicating a possible crosslinked structure.

The particle size was investigated as a function of deposition time, the time duration for the electrospun mat in the metal ion solution. Figure 4 (inset) illustrates the cumulative frequency distributions of the particle diameters obtained from five different deposition times. The size of silver particles is in range of 35-55 nm. Increasing coating time broadens the size distributions. Particle size increases with increasing coating time. The particles were limited to grow to maximum 60 nm. The controlling mechanism of silver particles size on nanofibers is unclear. Two substrates having different chemistry, PGMA and P(AN-GMA), were used to investigate Ag particles diameter. No striking difference was observed between the size of silver particles obtained on PGMA and P(AN-GMA) mats. Figure 4 illustrates the average size of the particles reduced during five different deposition times. In homopolymer, the density of active site (oxirane group) for hydrazination is two times higher than the copolymer.

The centre of crystal nucleation is the hydrazinated oxirane molecules on the fibers surface. The density of particle attachment is controlled by the formation of reactive sites on surface. Successful hydrazination reaction may increase nucleation centres and therefore the particle distance become shorter. The nanoparticles appeared on the nanofibers within few seconds after the electrospun mat was immersed into the deposition solution. Silver atoms nucleate not only on fiber surface but also on space between nanofibers, as presented on Figure 5.

The uncontrollable crystal growth raises the particle agglomerations that link fibers to make nanobundles as can be seen in Figure 5. As a result of fiber bundling the pores between electrospun fibers became larger, the surface area to volume ratio of both electrospun fibers and metal nanoparticles shrunk. At this

stage it is speculated that the nucleation centres of the two neighbouring fibers which are close each other adhere and crystal growth bridges the two fibers.

In summary, a new approach to synthesize large surface area polymer-metal nanocomposite is presented. It is a simple, inexpensive way to generate metal-coated electronic fibers at ambient conditions by employing solution processing techniques. The fibers and the particles have nearly uniform diameters. The metallized nanofibers can be perhaps used as the precursor of silver nanotube.

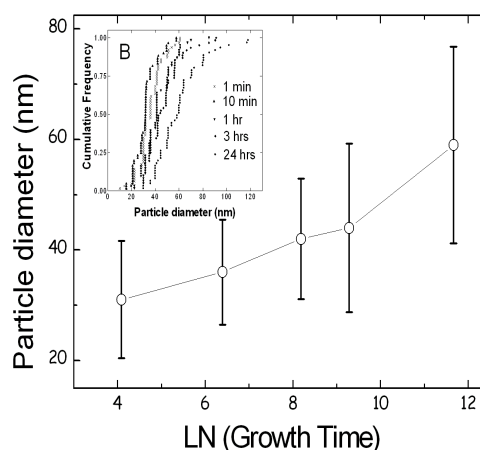


Figure 4. The particle sizes as a function of logarithm of deposition time in seconds P(AN-GMA). Cumulative distributions of particles are given as the inset.

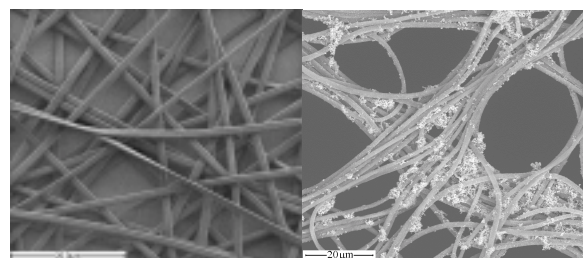


Figure 5. A- The electron microscope image of PGMA nanofibers obtained from 30 wt% solution in DMF at 1.53 kV/cm. **B-** Electron microscope images of Ag coated P(AN-GMA) nanofibers. Coating time is 2 minutes.

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