Physical and thermal properties of nano lead oxide loaded electrospun PAN nanofibres

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Electrospun nanofibres of polyacrylonitrile (PAN) and PAN mixed nano lead oxide (n-PbO) matrices have been produced. With the increase in concentration of nano lead oxide in the electrospinning matrices, the diameter of fibres is found to increase. The tensile strength of electrospun matrices increases up to 0.8 wt% incorporation of nano lead oxide but with further increase in nano lead oxide the tensile strength of the web decreases. The conductivity of the parent sample is found to be better compared to that of sample mixed with n-PbO.

Keywords: Electrospinning, Nanofibres, Nano lead oxide, Polyacrylonitrile fibre

1 Introduction
Electrospinning has been one of the promising routes to produce fibre under submicron diameter range. The very large surface area to volume ratio of the electrospun fibres makes them optimal candidates for many important applications.

The major applications in which these nanofibres matrices find applications are tissue engineering, air filters, water filters, solar cells and batteries. Electrospinning with various polymers and solvent combination has been carried by various researches.

Among the various polymer, electrospinning of PAN has evoked considerable interest as it finds interesting application such as super absorbent, precursor for carbon fibres and other biomedical application such as drug delivery and artificial muscles. The study on PAN electrospun fibres mixed with various metal oxides such as TiO₂, ZnO, nano silver, metals and carbon nano tube has already been reported.

The addition of functional materials to PAN has provided ample leverage to use the matrices in various applications ranging from hydrogen storage to antimicrobial fibre. PbO nano powder and particles have been used in magnetic resonance, imaging, gamma radiation protective clothing and X – ray sensing applications. In the present study, efforts have been made to study the physical and thermal characteristics of PAN nanofibre mixed with various concentrations of lead oxide nano particles.

2 Materials and Methods

2.1 Preparation of Nano Lead Oxide
Nano lead oxide was produced by facile wet synthesis method. In this method, aqueous solution (using de-ionized water) of 50mL of 0.5 M lead acetate was added to an aqueous solution of 50mL sodium hydroxide (1M) in a beaker with vigorous and continuous stirring. Upon addition of lead acetate, the solution initially became cloudy and after stirring for 30-45 min, the precipitate was formed which was then allowed to settle down. The supernatant was filtered using whatmann filter paper and filtrate was dried in a drying oven at 90°C. The sample was then removed from filter paper and powdered with the help of a mortar and pestle.

2.2 Electrospinning
The polymer solution (10 w/v% of PAN- co-methyl acrylate procured from Sigma Aldrich (94:6), molecular weight 150,000, in DMF) was taken in a syringe, which was mounted on pump (KD Scientific). The tip of the needle was connected to high voltage source (gamma high voltage), which can generate DC voltage up to 30 kV. Rotating drum wrapped with aluminum foil was placed as a grounded collector. The applied voltage between the tip and the collector was set at 20kV with a tip-to-collector distance of 10 cm. The fibres were collected...
on the aluminum foil in the form of nonwoven matrices. The diameter of fibres was analyzed using ‘Image J’ software.

2.3 Test methods
The X-Ray powder diffraction (XRD) analysis was performed with a SEIFERT JSO DEBYEFLEX 2002, German make, diffractometer equipped with a conventional X-ray tube Cu kα1 radiation (λ = 1.5406 Å) power condition (40 KV/30 mA). The XRD pattern was measured in the 20 range 10°-70° with the step size of 0.02° and 30 s counting per step at room temperature. The Fourier transform infrared spectroscopy (FTIR) was carried out using Bruker optik GMBH FTIR spectrophotometer in the range 500 - 3500 cm⁻¹. KBr pellets mixed with the sample were prepared and used for testing. The tensile strength (g/tex) of the electrospun fibre mat of 40 mm width was measured in Instron 3309 Universal tester. The gauge length was set at 5 cm and the testing speed was kept at 10 mm/min.

The morphologies of electrospun nanofibres were observed by scanning electron microscope (SEM, HITACHI) after being ion sputter coating with gold target. The diameters of electrospun precursor were analyzed with an image analyzer. Thermo gravimetric analysis (TGA) of electrospun fibres was performed from 50°C to 800°C at 20°C min⁻¹ heating rate using TA Instruments Q 500 in nitrogen environment. The electrical conductivity (S/cm) of prepared sample was measured at room temperature using four-point probe developed in-house in our laboratory.

3 Result and Discussion
3.1 X-Ray Diffraction Studies and FTIR Analysis
The formation of nanostructure lead oxide was studied using X-Ray diffraction (XRD). The XRD pattern for n-PbO is shown in (Fig. 1). The phase purity of the prepared tetragonal n-PbO can be clearly seen and all diffraction peaks are perfectly indexed to the tetragonal PbO structure. No characteristic peaks of impurities were detected. The broadening of the peaks indicated that the particles were of nanometer scale.

The FTIR studies of n-PbO, pristine PAN and n-PbO loaded PAN sample are shown in Figs 2(a)-(c). The FTIR spectrum of n-PbO carries peaks due to C-H stretching vibrations at 2938, 2876 and 2823 cm⁻¹. The characteristic C≡N vibration is seen at 2242 cm⁻¹ and CH₂ bending vibrations are seen at 1363 cm⁻¹ and 1448 cm⁻¹. In addition to this characteristic peak of PAN, the peak at 1729 cm⁻¹ is due to the carbonyl group of the co-monomer. The FTIR spectrum of n-PbO loaded PAN displays same bands as that in pristine PAN [Fig. 2 (b)], but in addition to that certain group of peaks below 900 cm⁻¹ indicate the presence of PbO vibration.

3.2 Tenacity
The tenacity (g/tex) of the pristine and n-PbO loaded samples is given in Fig. 3. It can be seen that with the increase in n-PbO content upto 0.8 wt% there is a slight improvement in tenacity but with the further increase in n-PbO the strength of specimen drops. The increase in tenacity upto 0.8wt% addition of n-PbO may be fit due to reinforcing effect and the particles may act as filler. However, with further increase, the compatibility of polymeric chain gets affected despite the reinforcing effect. Similar observation has also been reported for grafting acrylonitrile onto PP monofilament.
3.3 Surface Morphology of Electrospun Matrices

The surface morphology of the electrospun matrices, characterized using SEM, is presented in Fig. 4. Further the diameter of the fibre is measured using ‘Image J’ software and the results are presented in Fig. 5. It can be seen that with the increase in concentration of n-PbO the diameter of the fibre increases. This may be due to the interaction of the lead oxide with the polymeric solution which affects the charge density of the jet, thereby increasing the instability of jet which results in fibre with increased diameters.

However, the uniformity in fibre is observed in nano lead oxide loaded samples compared to that of parent samples. This may be due to the plasticizing effect of n-PbO, similar to that of a surfactant such as PEG\textsuperscript{15,16}.

3.4 Thermogravimetric Studies

The TGA thermograms of the pristine PAN and n-PbO oxide loaded PAN samples are presented in Fig. 6. It can be seen that with the increase in loading of the PbO nanoparticles, the profile of curve is distinctly changed except at 0.4% loading. The increase in thermal stability of the polymer at 0.4% loading may be due to reinforcing effect of the n-PbO particles, however with the increase in loading concentration the disruption of arrangement of polymeric chain takes place, thereby leading to poor thermal stability. However, it is interesting to note that at higher n-PbO loading (1.6%), there is drastic decrease in weight and moreover the residue of the polymer is almost zero. This may be due to the disruption of the polymer chain interaction, thereby preventing the cyclization reaction. Moreover it should be noted that the PAN nanofibres generally
have lower thermal stability due to its nano dimensions and increased surface area.

3.5 Conductivity Measurement

The conductivity of n-PbO loaded PAN fibres is found to be lower compared to the control sample (Fig. 7). The conductivity of the mat depends on the microscopic and macroscopic conductivities of polymer and oxides inside the polymer matrix. Both the microscopic and macroscopic conductivities depend upon the orientation of the particles and its dispersion. In order to have better conductivity, the nanoparticles should have good compactness and microcrystalline orientation.

4 Conclusion

The nano lead oxide synthesized has been incorporated in PAN fibre and following results are obtained:

4.1 The diameter of n-PbO loaded nanofibres is found to be high compared to that of pristine PAN and the fibres are uniform in nature.

4.2 The thermal stability of n-PbO loaded sample is found to be lower compared to the pristine PAN.

4.3 The tensile strength of n-PbO loaded nanofibres sample increases up to 0.8 wt% of added PbO and then it decreases.

4.4 The electrical conductivity of n-PbO loaded nanofibres sample decreases drastically compared to the pristine PAN sample.

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