Development of Keratin Based Poly Vinyl Alcohol (PVA) Electrospun Nanofibrous Mat from Wool Waste for Air Filtration

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Abstract—In this article, we have prepared the PVA nanofibers with Keratin by electrospinning technique and physicochemical, and filtration property of PVA/keratin nanofibers were studied. PA6/keratin nanofibers composite were prepared with different proportions of keratin with respect to PVA, i.e.,1:0, 1:1, 1:2, 2:1. PVA/Keratin nanofibers were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and Field emission scanning electron microscopy (FESEM). FTIR showed that Keratin gets compatible with PVA. XRD patterns illustrated keratin was in crystalline nature and helps to increase the crystallinity nature of PVA nanofibers. FESEM images showed the uniform formation of nanofibers. The nanofibers diameter was found to be below than 100 nm in size with small pore size. Nanofibers filtration efficiency against a particulate matter was obtained more than 98%.

Keywords—Keratin, Polyvinyl alcohol, electrospun nanofibers, wool waste, etc.

I. INTRODUCTION

Wool is the obtained from sheep and other animals; Wool mainly consists of protein together with a few percent lipids. In this regard, it is chemically quite distinct from the more cotton textile fiber, which is mainly cellulose. \cite{1} Management of waste wool is a problem related to sheep farming. Wool is very coarse and contains a lot of kelps (dead fibers), so that it is practically unserviceable for textile uses, and represents a byproduct which is mostly disposed of. The waste wool can be recycled into different forms like fertilizers, extraction of keratin, etc.

Keratin is an abundant nonfood protein which is the major component of wool, hair, feathers, horns, and nails \cite{2}. Wool contains up to 95\% by weight of pure keratin. Wool keratin has a molecular weight ranging from 45 to 60 kDa of the microfibrils from the cortical cells to 6–28 kDa of the protein from the matrix. At present, wool keratin has been prepared into the films \cite{3}, sponge scaffolds \cite{4}, and nanofibers \cite{5} and mainly used for biomedical application and adsorption. Wool keratin is difficult to electrospin into nanofibers because of its low molecular weight and brittle property, therefore the requirement of the carrier or flexible material such as a polymer to obtained nanofibers of keratin. Nanofibers are prepared majorly with electrospinning techniques. In general, electrospinning apparatus is made up of a high voltage supply, a capillary tube with a pipette or needle of small diameter, and a metallic collector.

Nanofibers are one of the unique materials which have been studied as such or in combination with other materials such as textiles for air filtration. Electrospun nanofibers have been explored for the adsorption of volatile organic compounds (VOC) present in the air by various authors. \cite{6-9}.

In this work, the wool keratin was extracted from the deccani wool waste, and nanofibers are generated with PVA with different ratios of keratin to PVA. The PVA/keratin nanofibers were fabricated by using electrospinning technique. PVA/keratin nanofibers could be interesting candidates for air filtration to remove out the toxic, unwanted particulate matters available into the air.

The blend solutions of PVA/keratin were electrospun to produce nanofibers. The physicochemical, as well as filtration properties of the blend nanofibers, were investigated.

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II. MATERIALS AND METHODS

Deccani wool waste was used for keratin extraction. Petroleum Ether, Urea, 2-Mercaptoethanol, sodium Dodecyl sulfate (SDS), Cellulose Dialysis Tubing (molecular weight cut off 12000-14000Da) obtained from Himedia laboratories (Mumbai, Maharashtra), Poly Vinyl alcohol (PVA) procured from S.D fine Mumbai.

2.1 Extraction of Keratin from Wool Waste: Keratin protein was extracted from wool waste fiber according to the method reported previously [10]. Briefly, wool fibers were soaked in petroleum ether for 4 hours to de-waxing it. Then the protein was extracted by incubating 10 grams of wool with a mixture of 0.2 M SDS, 8 M urea and 2 mercapto ethanol at 60 °C for 5 hours. The solution was then filtered to remove the un-dissolved wool fiber and thoroughly dialyzed against distilled water using cellulose tubing to remove the chemicals and then the aqueous keratin solution was obtained. The keratin solution was poured into a petri dish and placed it in the oven for 2 days and to get Keratin powder.

2.2 Preparation of PVA/keratin nanofibers: The PVA/Keratin prepared at 1:0, 1:1, 2:1, and 1:2 (coding P1, P2, P3, and P4 respectively), concentrations ratios in de-ionized water and electrospun at a 15cm working distance to ensure that the nanofibers were dried. The applied voltages were between 15-30 kV. About 2 mL of the polymer solution was placed in the syringe. The tip was positively charged by the generator. When a steady voltage was reached between the tip and collector, the delivery pump switched on and fed the fixed flow 2 ml/hr of the solution through the capillary, and the electrospinning process started. The process was stopped after about 10 min. During the electrospinning process, Environmental conditions were kept in check; in particular, the temperature was ranged from 20 to 25°C and the relative humidity was in the range of 35–55%.

III. CHARACTERIZATION

3.1 UV Visible Spectroscopy: UV Visible spectroscopy of powdered keratin was obtained by making the solution in water and analyzing UV Visible spectra with the help of Specord 201 Analytik Jena Germany.

3.2 Fourier Transform Infra-Red (FTIR) Analysis: Fourier transforms infrared (FTIR) spectra of keratin and PVA/keratin nanofibers were obtained by using the ATR technique (Attenuated Total Reflection). An infrared spectrum of keratin was recorded from 5000 to 500 cm⁻¹ using Alpha Bruker spectrophotometer Germany.

3.3 Differential Scanning Calorimeter (DSC) Analysis: Differential scanning calorimeter (DSC) analysis of keratin after conditioning the samples and PVA/keratin nanofibers at 24°C, 65% R.H was performed from 30°C to 500°C, at 10°C/min using instruments DSC 3 Mettler Toledo, Switzerland. The instrument was calibrated by an indium standard, and the calorimeter cell was flushed with 40 ml/min liquid nitrogen.

3.4 X-Ray Diffraction Analysis: Crystalline nature was judged by Bruker, D8 ADVANCE (Bruker Corporation, Tokyo, Japan) X-ray powder diffractometer (XRD) using monochromatic CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The scan rate was 50/min between the angles 5-80°.

3.5 Scanning Electron Microscopy: Surface morphology was observed using scanning electron microscope (SEM), HITACHI S-4800, operated at 5 to 15 Kv. Nanofibers was cast onto carbon tape and dried at room temperature. Prior to analysis sample was coated with gold to avoid degradation or burning due to high power.

3.6 Air Permeability: This test method covers the measurement of the air permeability. The rate of air flow passing perpendicularly through a known area under a prescribed air pressure differential between the two surfaces of a material of textile fabrics and is applicable to most fabrics including woven fabrics, Non woven fabric, air bag fabrics, blankets, napped fabrics, knitted fabrics, layered
fabrics, and pile fabrics etc. Nanofibrous mat comes with Non woven fabric. Therefore it's important to evaluate air permeability of nanofibrous mat. Determination air permeability of keratin-based nanofibrous mat under designated pressure analyzed standard ASTM D 0737 by applying pressure 125pa and test area 38cm2 using Air permeability tester MO211A SDL ATLAS Hong Kong.

3.7 Filtration Efficiency (Dop) Test: Filtration efficiency with pressure drop evaluated by the PALAS2010 instrument was 0.3μ-4μ particle size dust/aero-gel passed through nanofibers coated membrane and evaluate % retention of solid particles and pressure drop. DOP/PAO testing is a very quick process that tests the integrity of the High-Efficiency Particulate Air filter using DOP or PAO solutions in their operational conditions. These solutions generate a gas type smoke and then generate gas particles that will be greater than 0.3 microns.

IV. RESULTS AND DISCUSSION

4.1 UV Visible Spectroscopy:

![UV visible spectra of extracted keratin](image1)

Figure 1: UV visible spectra of extracted keratin

UV-Vis absorption measurement is a very simple method to explore the structural change. Keratin solution shows λmax at 273 nm. The UV-Vis absorption of keratin is shown in fig 1. Keratin absorbs mainly in the far UV but has an absorption tail out as far 380nm. The wide peak in the region 250-280 nm. The main chromospheres absorbing in the UV region are aromatic amino acids, tryptophan, tyrosine, and phenylalanine, which are present in the keratin chain.

4.2 FTIR Analysis:

![FTIR Spectra of Keratin and PVA /Keratin nanofibers](image2)

Figure 2: FTIR Spectra of Keratin and PVA /Keratin nanofibers

The FTIR spectra of keratin and Keratin/PVA nanofibers with different proportions are shown in fig 2. from the FTIR spectra indicated the location of characteristic absorption peaks of keratin available in nanofibers. The characteristic absorption band for peptide bonds (–CONH–) was seen. The vibrations in the peptide bonds can be attributed to Amide A, amide I, II, III. The amide A band, which falls at 3327.12 cm⁻¹ is due to the stretching vibration of N–H bonds[11]. The amide I
band due to C–O stretching vibration occurs in the range of 1700–1600 cm\(^{-1}\). Sharp peak was observed at 1656.8 cm\(^{-1}\). The amide II, which falls at 1544.47 cm\(^{-1}\) is related to N–H bending and C–H stretching vibration. The amide III band (1220–1300 cm\(^{-1}\)) was observed at 1245.18 cm\(^{-1}\) as a sharp peak [12-13]. The carbohydrate moieties band (1000–1100 cm\(^{-1}\)) was observed at 1083.10 cm\(^{-1}\) as a sharp peak.

The absorption band at about 3323.12 cm\(^{-1}\) in pure keratin exists in nanofibers. The peak at 2923.88 cm\(^{-1}\) and 2854.45 cm\(^{-1}\) was seen, which is related to —H stretching and bending vibration of PVA. Amide I and Amide II present in nanofibers where one additional carbonyl stretching vibration was observed at 1690 cm\(^{-1}\) peak arise due to the presence of PVA; The amide III band was observed at 1245.18 cm\(^{-1}\) in nanofibers.

4.3 DSC Analysis:

DSC is the most popular thermal technique, which measures the heat absorbed or liberated during various transitions in the sample due to temperature treatment. The DSC thermogram of keratin is shown in fig 3. The denaturation temperature observed around 56°C is due to water evaporation. The endothermic peak observed above 148°C is reported for α helix denaturation in keratin. The second endothermic peak for the wool keratin was observed at 224°C. Appreciably high thermal stability of the biomaterial would be an advantage for applications where thermal stability is important. DSC traces of the films dried at 70 °C for 24 h in an oven. Overall, the DSC plots of the pure keratin and the blended nanofibers correspond to partially crystalline structures. In fig. 3 shows the DSC curves, the endothermic peak at approximately 86.17°C can be attributed to the evaporation of bound water, representing the energy required to vaporize bound water present in the nanofibers, followed by another endothermic peak observed at about 189°C related to the crystalline melting (Tm) of nanofibers [14-15], and the peak area representing the crystalline of the nanofibers. PVA interferes with the keratin self-assembling, causing the protein chains to organize in a thermally more stable secondary structure.

![Graph](image)

**Figure 3**: DSC analysis of Keratin and PVA /Keratin nanofibers

4.4 X-Ray Diffraction Analysis:

X-ray diffraction spectra of extracted keratin shown in fig 4. In XRD spectra peak arise at 2Θ. 21.2° are an index for crystalline nature of keratin. XRD spectra clearly indicate the extracted keratin was in a highly crystalline state.

X-ray diffraction spectra of PVA/keratin blend nanofibers was shown in fig.4. In XRD spectra peak arise at 2Θ. 21.2° are an index for the crystalline structure of keratin. XRD spectra clearly indicate the extracted keratin was in a highly crystalline state. In case of PVA/keratin blend nanofibers intensity peaking at 2Θ. 21.2° increases due to the addition of crystalline keratin.
Figure 4: XRD analysis of Keratin and PVA/keratin nanofibers.

4.5 Air permeability Analysis:
Nanofibers were coated on the nonwoven fabric for the filtration application purpose. Therefore there was a requirement to analyze the air permeability of nanofibers coated fabric. 10 samples were tested and taken the mean of them. Results showed in table no 10. The nonwoven fabric has air permeability 25.5cfm at pressure 125pa where in case of nanofibers coated fabric air permeability going to decreased air permeability. Reduction in air permeability arises due to the nanofibrous mat which restricts the flow of air pass through the fabric. The fabric has pore size larger 100 times more than a nanofibrous mat, but in case of nanofibrous mat pore size is very less up to 100nm, but the density of pore was numerous which helps to pass the air through the fabric by reducing as possible resistance. Results show the air permeability of nanofibers is similar to each other in nonkeratin and keratin based nanofibers.

| Sample       | Air permeability (cfm) |
|--------------|------------------------|
| Nonwoven PP fabric | 25.5                   |
| P1           | 18.6                   |
| P2           | 18.7                   |
| P3           | 18.4                   |
| P4           | 18.7                   |

4.6 Filtration Efficiency Analysis:
Prepared nanofibers coated fabric was sent to DRDO Gwalior for testing. DOP test performed at Defence Research Development and Establishment (DRDE) Gwalior. Test performs with the standard procedure at DRDE. The particulate matter (aerogel) passed through face mask at 95 L/m and evaluated the filtration efficiency. Obtained result shows excellent filtration efficiency 97-98% due to the presence of nanofibers. Nanofibers were played an important role in filtration; nanofibrous mat contains very small pores to 100nm which helps to restrict particulate matter which will more than 100nm. The densities of nanopores are numerous due to that air can easily pass through the membrane, but particulate matter gets restricted. The maximum density of nanopores helps to maintain pressure drop.

| PVA/Keratin Nanofibers | Particulate counts | (%) Filtration efficiency | Pressure drop(ΔH) mmwg | Air flow |
|------------------------|--------------------|----------------------------|------------------------|----------|
| Inlet Count (C1)       | Outlet count (C2)  |                            |                        |          |
| P1                     | 146863             | 2468                       | 98.31                  | 16       |
| P2                     | 156941             | 1999                       | 98.72                  | 19       |
| P3                     | 148532             | 1975                       | 98.67                  | 19       |
| P4                     | 146571             | 1956                       | 98.66                  | 18       |

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4.7 Surface Morphology Analysis:

Surface morphology of prepared nanofibers observed with the help of Scanning electron microscope. The sample P2 showed highest filtration efficiency and analyzed under SEM for determination of surface morphology of nanofibers. Surface morphology of nanofibers showed in fig 5 clear view of the mesh-like nonwoven structure of with the fiber diameter below than 100 nm. This mesh-like structure gives excellent filtration efficiency for particulate matter present in the air.

![Figure 5: SEM image of PVA/Keratin nanofibers](image)

V. CONCLUSION

Keratin extracted from deccani wool waste and blended with PVA at different ratios; The electrospinning process appeared stable and successful for PVA/keratin blend solutions. All the nanofibers were found to be smooth and bead-free with favorable compatibility between keratin and PVA. Formation of hydrogen bonds between the two components was confirmed by FTIR spectroscopy. The crystallinity of the nanofibers improved with the incorporation of keratin, but the orientation of nanofibers was favorable to crystallization. The filtration efficiency of PVA/keratin nanofibers were shown more than 98% filtration efficiency. Overall, the present work demonstrated the possibility to incorporate Keratin into nanofibers that have the potential to be applied in the filtration industries.

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VII. REFERENCES

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