Development of PAN nano fibrous filter hybridized by SiO_2 nanoparticles electret for high efficiency air filtration

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ABSTRACT

Airborne dust particles has become an ever-increasing environmental concern and is also a threat to public health, leading the way in the development of fibrous materials with fascinating features like high filtration efficiency and low pressure drop. To enhance the filtration efficiency of fibrous material, particularly for submicron- sized particles, here we report a promising and versatile electret polyacrylonitrile-silicon dioxide (PAN- SiO_2) fibrous membrane, considering the higher particle capture efficiency for an electret filter compared to a conventional fibrous filter. The chemical bond nonwoven and spun bond nonwoven substrates were used as support material to enhance the mechanical property and also the handling property of the as developed electrospun nanofibrous membrane. In this research work, SiO_2 is identified as the potential material for developing electret filter due to its dipolar nature. The concentrations of SiO_2 nanoparticles (NPs) were varied to achieve better filtration efficiency. The morphology of fibrous membrane, its air permeability, areal density and thickness properties were analyzed as per standard test methods. The filter fabrics were developed and its filtration performance and pressure drop were also characterized.

KEYWORDS : Electrospinning, polyacrylonitrile, SiO_2 Nanoparticles, Submicron particle.

1. INTRODUCTION

The use of textile fabrics (woven and non-woven fabrics) as filter medium is one of the ways to overcome the problem caused due to air pollution[1,2]. In case of air filtration, nanofibrous non-woven mat plays the most important role for filtering sub-micron range of aerosol particles due to the benefit of their reduced fibre diameter,

J. Polym. Mater. Vol. **35,** No. 3, 2018, 317-328

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DOI : https://doi.org/10.32381/JPM.2018.35.03.6

large surface area to volume ratio, high permeability, low basic weight, small pore size and randomly aligned fibrous [3-5]. Nanofibres with the nonwoven structure are mostly produced using electrospinning technique, which uses electrostatic force to spin fibres. The selection of suitable polymer is very critical in determining the quality of filter being developed through electrospinning. There are many types of polymers (e.g. polyvinyl alcohol (PVA)[6], Polyvinylidene fluoride (PVDF)[7], polyurethane (PU)[8], polysulfone (PSU)[9]) being explored by researchers for electro-spinning nanofibrous mat with superior performance for novel applications ranging from environmental protection to bio-medical applications [10].

When it comes to filtering of particles by the filter medium, the particles capture mechanisms can be broadly classified into two, mechanical (Interception, Impaction and diffusion) and electrostatic mechanism (Coulombic attraction and dielectrophoresis)[11,12]. Among them the particle capture efficiency of an electret filter (electrostatic charge induced filter) employing electrostatic capture mechanism is much better and efficient, with minimum increase in pressure drop. Moreover, the incorporation of NPs into polymeric materials will enhance the mechanical properties of the composites. For e.g. carbon black, nano-particular filler was used in the rubber industry to increase the mechanical strength of rubber composites [13]. This concept is applied to strengthen the electrospun nanofibres used in membrane technology. In another work, researchers tested different electret NPs including Boehmite, SiO_2, silicon nitride, barium titanate with PEI fibres for high-performance air filtration, and the membrane doped with the SiO2 NPs showed the best performance [14]. Daehwan Cho et. al. reported their study on nanofibrous filter media based on PAN nanofibres with and without TiO_2 NPs. It was clearly shown that using metal oxide NPs covering the polymeric nanofibres, very high air filtration efficiency and low-pressure drop was achieved [15]. This is either due to the increase in surface area of the membrane or due to the strongly influence of electrostatic interactions between dust particles and nanofibres or both the factors put together.

Following this criterion in our study, Silica (SiO_2) NPs as a novel nanofiller in the membrane technology were selected to enhance the filtration efficiency of air filters by exploiting the electret nature of SiO_2. The addition of these silica NPs increased the surface roughness, thereby increasing the stagnation region, and facilitating the air penetration through the membranes [11]. Many researchers have already used silica nanoparticles in filtration applications. Xue Mao et. al. in the year 2012 developed a new class of flexible and thermally stable silica nanofibrous membranes by the combination of electrospinning and sol–gel methods[16]. The silica produced using this method is not porous. In our study, the synthesized SiO_2 NPs are highly porous (mesoporous SBA-15). If the NPs have porous structure then the highly porous structure (80% or more) of the electret filter media ensures that the dust particles are captured through the depth instead forming a cake on the surface alone, leading to better particle holding capacity. This gives the filter a longer life by reducing the membrane fouling caused by early clogging of pores [17]. Also, we have used semi-crystalline and polar polymer with high dipole moment such as polyacrylonitrile (PAN) owing

to its high mechanical and fiber-forming properties, which can be exploited for the better removal efficiencies of ultra fine particles. The polar nitrile groups of PAN give it a higher dipole moment and piezoelectric property too [18,19].

With this in hand, the idea is to develop an electret filter with dipolar SiO_2 NPs (electrets) incorporated in dipolar PAN electrospun web supported by non-woven fabric for high-performance and high efficiency air filtration medium. Various physical and functional properties have been analyzed to identify its performance and then optimizing the filter medium accordingly.

2. MATERIALS AND METHODS

Materials : Polyacrylonitrile(MW 150,000 g/mol) was obtained from Sigma–Aldrich. Triblock copolymer (Pluronic123), TEOS (Tetraethyl orthosilicate), and HCl was purchased from SRL chemicals. All chemicals were of analytical grade and used without further purification. Pluronic123, TEOS, HCl and distilled water are the chemicals used to synthesis SiO_2NPs. Spun bond nonwoven fabric and chemical bond nonwoven fabrics are made of Polypropylene (PP) and used as support material with the areal density of 40 g/m^2 (GSM).

Spunbond process is widely used to produce nonwoven fabrics. The process involves extruding a thermoplastic fibre-forming polymer to form fine filaments. Then the filaments are collected in the form of a web, followed by thermal bonding the fibres to make spunbond nonwoven fabric [20]. And in chemical bonded nonwoven fabrics binders (adhesive materials such as acrylic resin) are used to hold the filaments together. After the binder is applied, the web is passed through hot rollers to cure the adhesive applied filament[21].

Principle of membrane construction: The idea is to construct a high performance filter medium with impressive durability and stability against the pressure it is subjected to while acting as an air filtration nanofibrous membrane. The nanofibrous filter membrane has been sandwiched between layers of non-woven support material. Considering PP non-woven fabric's durability, and hydrophobicity, it is used as support material for the electrospun nanofibrous filter membrane. The principle of construction of the nanofibrous air filtration membrane is shown in Fig. 1.

Experimental plan : The nanofibrous filter membrane for air filtration was developed using the electrospinning process and the schematic diagram is shown in Fig. 2. In our work, electrospun PAN nanofibrous membranes were reinforced by various concentrations of SiO_2NPs in order to improve their filtration properties by exploiting SiO_2NPs electret nature. These mesoporous SiO_2 NPs were synthesized using non-ionic block copolymer. All

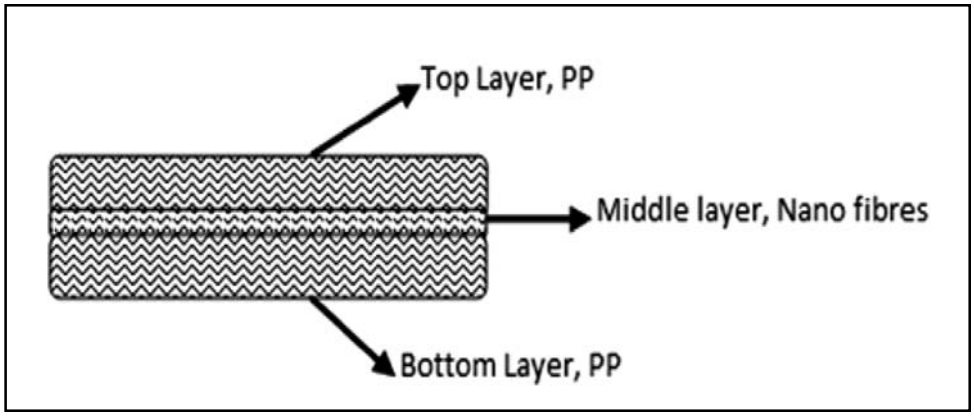

Fig. 1. Principle of construction of the nanofibrous air filtration membrane

PAN and PAN/ SiO_2 spinning solutions were electrospun at a voltage of 15 kV with a tip-to-collector distance of 15 cm. Each electrospun web was sandwiched between non-woven support material (spun bonded and chemical bonded) to improve the membrane's stability. The three-layered web was then bonded together using thermal bonding technique. All the as prepared samples underwent various characterizations.

Synthesis of SiO_2NPs: The mesoporous SiO_2 NPs SBA-15(Santa Barbara Amorphous type material-15) was synthesized as per our previous work[22,23]. A typical synthesis was started with dissolving 1g of Pluronic 123 in 145 ml of distilled water at 35° C, followed by the addition of 15 ml HCl (35%) to the solution. This mixture was then stirred with 3 g of TEOS at 200 rpm for 24 h. A Teflon-coated closed vessel was then used to heat the above mixture at 100° C for 24 h, without any kind of stirring. The resultant product was filtered and was thoroughly washed with water and ethanol, followed by the drying of solid product at 100°C. The combined washing using both solvents (water and ethanol) may increase the surface area of SBA-15 and is hence considered an important step in the synthesis of SBA-15[24]. To remove the copolymer, the dried solid powder (precalcined SBA-15) were calcined at 550° C for 6 h.

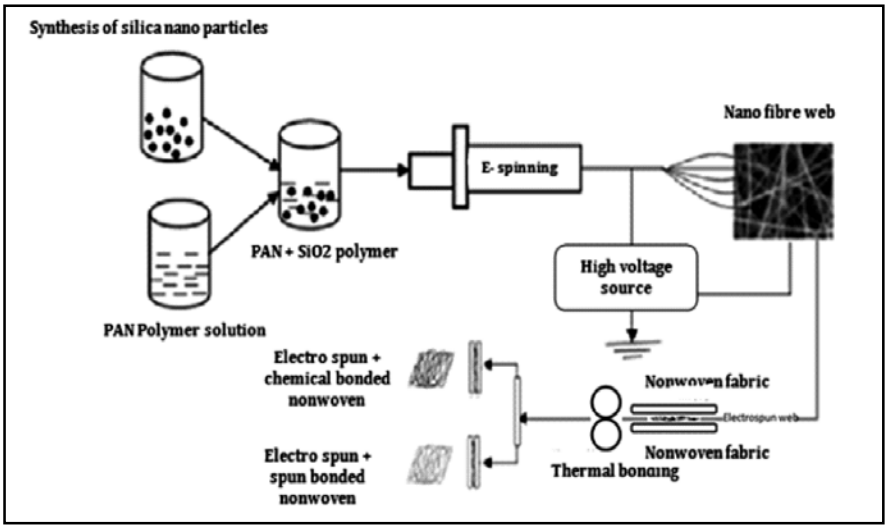

Fig. 2. Schematic diagram of the experimental method

Preparation of polymeric solution: Number of experiments was carried out with different blend ratio of SiO_2NPs/PAN to optimize the production of nanofibrous matrix. To start with, a viscous polymeric solution was prepared by mixing of 8 wt% of PAN in DMF with stirring for 3 h at room temperature. To this polymeric solution, SiO_2 NPs of 10, 20 and 30 wt% with respect to polymer weight was prepared individually. The as prepared polymeric solution was then subjected to the electrospinning to produce nanofibrous membrane.

Electrospinning of nanofibrous membrane: Nanofibrous web was produced from PAN solution containing 10, 20 and 30 wt % of SiO_2. The precursor solution (the PAN solution only and PAN/ SiO_2 solutions) was loaded into different syringes. The syringe is placed on a syringe pump which pumps the solution at a fixed flow rate of 0.5 mL/min to a stainless steel needle. A high voltage of 15kV was applied to the needle while the collector is grounded. Nonwoven support material such as chemical bond or spun bond fabric was placed in the collector screen with the distance of 15 cm from

the syringe tip. Before reaching the collector the solvent evaporates, and the PAN or hybrid PAN/ SiO_2nanofibres are collected as an interconnected web on the collector screen. All the experiments were conducted at room temperature with a relative humidity of 50%–55%.

Fabrication of PAN/SiO_2NPs hybrid membranes: In this work, PAN with SiO_2 incorporated electrospun web was prepared by electrospinning process. This electrospun web alone cannot solve the purpose and hence was integrated with chemical bond and spun bond nonwoven fabrics with a procedural work plan as shown in Table 1.

A total of 10 samples were developed with chemical bond fabrics (CBF) and spun bond fabrics (SBF) as the support material. The electrospun nanofibrous membranes were prepared as per the experimental plan given in Table 1. The prepared samples were bonded using Thermal Bonding Machine, which uses heat and high pressure (applied through two rotating rollers) to very feebly melt the polypropylene nonwoven fabric and bond the fibrous web together.

TABLE 1. Experimental plan for sample preparation

Substrate	SAMPLE	PAN (g)	SiO_2(g)
Chemical bonded nonwoven fabric	S1	-	-
	S2	0.4	-
	S3	0.4	0.04 (10%)
	S4	0.4	0.08(20%)
	S5	0.4	0.12(30%)
Spun bonded nonwoven fabric	S6	-	-
	S7	0.4	-
	S8	0.4	0.04 (10%)
	S9	0.4	0.08(20%)
	S10	0.4	0.12(30%)

3. Characterization of SiO_2NPs and nanocomposite fibrous membrane

Morphology of SiO_2NPs and electrospun membrane: The as synthesized SBA-15 using a self-assembly process was characterized using SEM. From the SEM images the morphology and the size of the SiO_2 NPs were studied.The morphology of the electrospun nanofibrous composite was analyzed using Scanning Electron Microscope (SEM) (S3400NSEM, HITACHI) at an accelerating voltage of 15 kV. Prior to the scanning under the SEM, the samples were sputter coated with gold using a Fine Coater (E 1010, HITACHI).

Characterization of nanocomposite fibrous membrane: As per EN ISO 9073-2(1996) standard, the thickness of the nonwoven fabrics were measured using Digital Thickness Tester under 0.5kPa of applied pressure with a presser foot diameter of 25 mm. ASTM D6242 was followed to measure the mass per unit area of nonwoven fabrics. The air permeability was tested using TEXTEST FX3300 Air Permeability Tester. The applied pressure was selected as 125 Pa and the fabrics were measured with an area of 38 cm^2 ring according to ASTM D737-04 test method.

Measurement of Filtration Efficiency: Filtration efficiency was measured using an Aerosol Filtration Efficiency tester as per the ASTM F2299 test method, and the experimental setup is shown in Fig. 3[25].

4. RESULT AND DISCUSSION

Characterization of SiO_2NPs: In the present work, mesoporous SiO_2NPs (SBA-15) with particle size range of 10 nm to 70 nm were prepared using block copolymer in an acidic media. The Scanning electron microscope (SEM) image (Fig 4 (a)) revealed the spherical shape of SiO_2NPs evenly distributed throughout the sample and having a very narrow particle size distribution. Whereas, figure 4(b) shows the Transmission electron microscope (TEM) image of SiO_2NPs revealing long cylindrical pores.

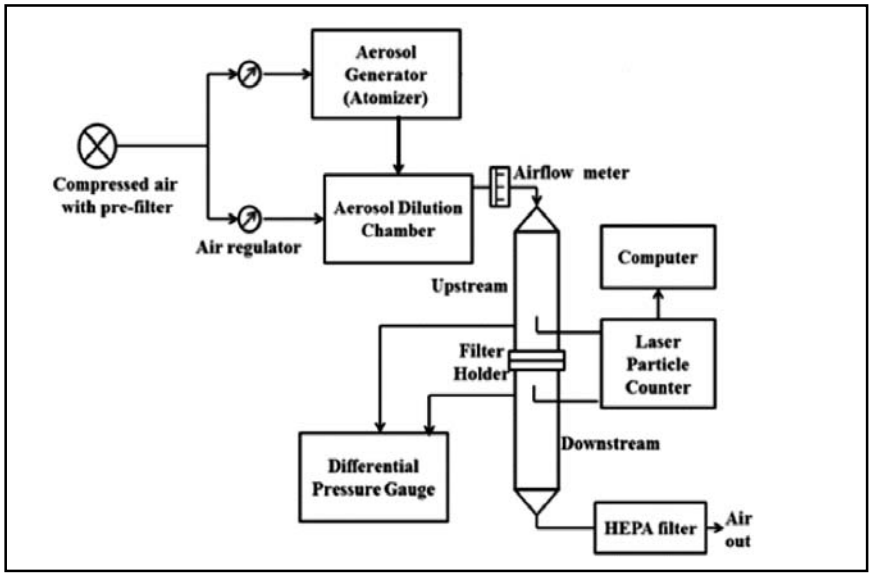

Fig. 3. Schematic diagram of Filtration Efficiency Tester[25]

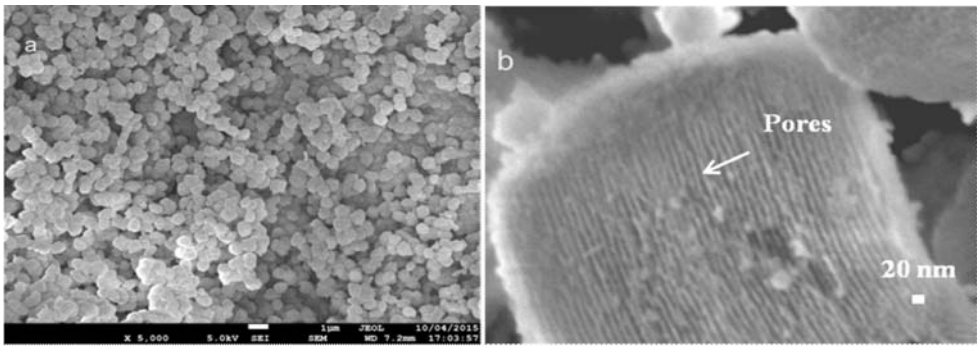

Fig. 4. (a) Scanning electron microscope image of SiO_2 NPs
(b) Transmission electron microscope image of SiO_2 NPs

Morphology of SiO_2/PAN nanofibrous membrane: PAN and PAN/ SiO_2 NPs electrospun web of different SiO_2NPs concentrations of 10, 20 and 30 wt% were characterized by SEM, and its images are shown in Fig. 5 (a) (b) (c) and (d) respectively. The fibres are having uniform surfaces and the diameter of the fibre increases while increasing the concentration of SiO_2 NPs. The diameters of the electrospun fibres were found to be in the range of 97, 183, 190 and 270 nm

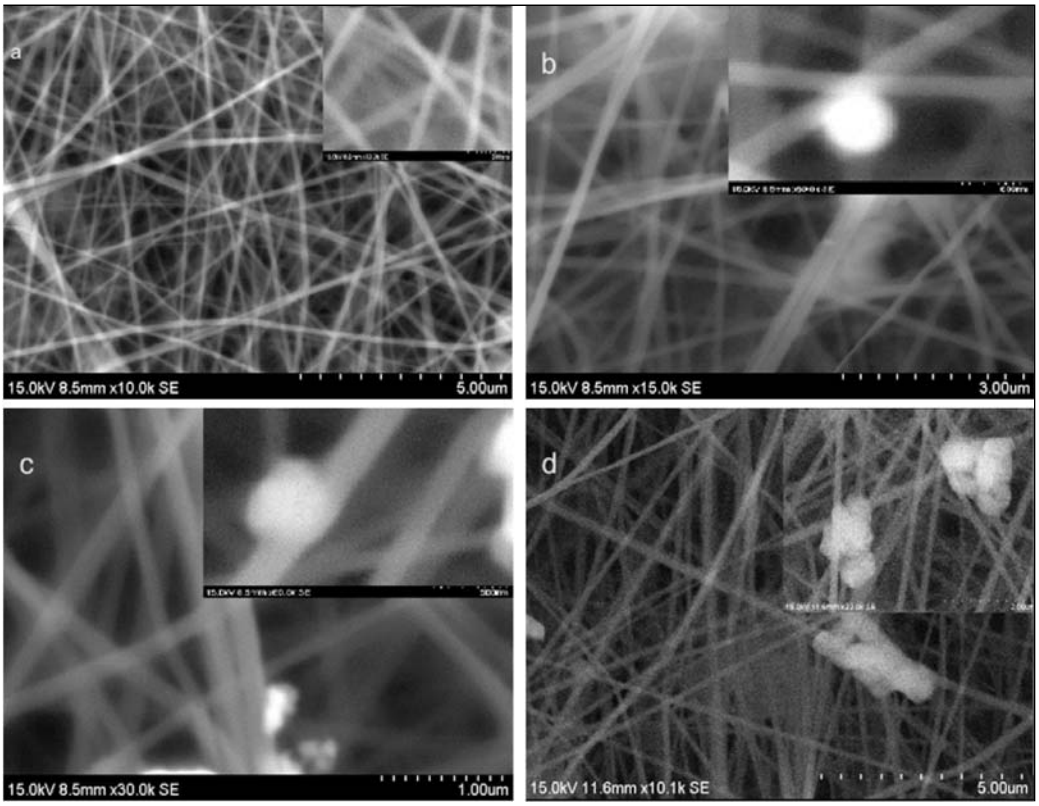

Fig. 5. (a) PAN (b) PAN with 10% SiO2 NPs (c) PAN with 20% SiO2 NPs (d) PAN with 30% SiO2 NPs

respectively. In addition, there is more bead formation as the concentration of SiO_2 NPs is increased in the polymer solution.

Properties of nanofibre composite membrane: The physical property of nanofibre composite membrane is given in Table 2. The thickness and areal density of the nanofibre composite membrane were increased while increasing the SiO_2NPs concentration in the polymer solution and also it influences the air permeability of nonwoven fabrics. The air permeability of nonwoven fabric will obviously decrease with increase in density and sample thickness. Air permeability is higher when

using spun bond nonwoven fabric support material compared to chemical bond nonwoven fabric as support material. But in general, in both the cases due to thermal bonding the polymer will melt and will block the path slightly, reducing the air permeability. From the study we have observed that the air permeability of the fabric reduces while increasing the mass per unit area and thickness.

But as the wt % of SiO_2 is increased, we could witness more beads formation leading to increase in diameter of nanofibres that might most probably result is increasing the air permeability. Hence, in case of sample 5 and sample 10 with SiO_2NPs of 30%; the air permeability has increased a bit when compared to sample with 20 wt % SiO_2NPs.

TABLE 2. Physical properties of nanofibre composite membrane

Sample ID	Sample description	Thickness (mm)	GSM	Air Permeability ($cm^3/cm^2/s$)
S1	CB only	0.230	64.2	49
S2	CB + PAN	0.310	66.3	2.23
S3	S2+10%NP	0.356	68.2	0.84
S4	S2+20%NP	0.368	69.3	0.44
S5	S2+30%NP	0.372	70.8	0.51
S6	SB only	0.410	68.5	172
S7	SB + PAN	0.412	70.2	6.27
S8	S7+10%NP	0.415	71.9	3.38
S9	S7+20%NP	0.424	73.2	2.81
S10	S7+30%NP	0.436	75.1	4.12

Filtration efficiency and pressure drop

The filtration efficiency of nano SiO_2 incorporated membranes has been higher than the other membranes and it is shown in Table 3. The incorporation of SiO_2NPs increases the filtration efficiency due to dipolar nature of SiO_2 particles. NPs incorporated membrane shows higher filtration efficiency. While further increasing the concentration of SiO_2 NPs results increase in fibre diameter and also bead formation in the structure of fibre. The filtration efficiency of SiO_2 NPs incorporated membranes (S3, S4, S5, S8, S9, S10) has been higher than the other membranes (S1, S2, S6, S7). S1 and S6 are filter membrane made only with chemical bond fabric and Spun bond fabric respectively and it is shown in Fig. 6. These two samples show the least filtration efficiency. With samples S2 and S7, there is a nanofibrous layer in between the nonwovens. With the incorporation of SiO_2NPs filtration efficiency increases impressively, due to the dipolar nature of

SiO_2NPs. Of the three different SiO_2 concentration in PAN solution, 20 wt% of SiO_2NPs incorporated membrane showed higher filtration efficiency. While further increasing the SiO_2 NPs to 30%, resulted in increase in fibre diameter and also resulted in the formation of beads on the fibres, and it lead to decrease in filtration efficiency.

TABLE 3. Filtration efficiency of samples

Particle size	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
0.3	1.34	49.57	93.61	93.83	91.15	40.04	76.26	79.48	97.18	84.4
0.5	8.24	69.58	99.1	99.19	98.36	56.67	91.33	93.78	99.58	95.58
0.7	19.65	72.74	99.77	99.8	99.51	63.46	95.83	98.35	99.87	97.41
1	29.96	80.16	99.84	99.9	99.78	68.39	96.67	99.29	99.93	98.82
2	51.22	87.06	99.91	99.96	99.88	78.09	97.96	99.87	99.97	99.8
3	77.61	80.4	99.92	99.99	99.89	90.19	89.95	99.99	100	99.98
Overall Filtration Efficiency	31.34	73.25	98.69	98.78	98.1	66.14	91.33	95.13	99.42	96
Pressure Drop	1.5	3	15	17.5	9	2	5	5	6	5.5

For high filtration efficiency, it is necessary that the membranes be endowed with smaller fibre diameter which results in reduction in pore size per unit area. In this work, with an increase in concentration of SiO_2 NPs the average fibre diameter increased from 97 nm to 270 nm. However S4 has higher filtration efficiency than S3, because of higher concentration of the electret SiO_2 NPs whereas compared to S4, S5 filtration efficiency has dropped down even with a higher concentration of SiO_2 NPs. This is due to the increase in fibre diameter with sample S5, which results in formation of bigger pore size thus reducing the filtration efficiency. Hence an optimal level of fibre diameter and NPs concentration places a major role in the filtration efficiency.

Sample S2 and S6 shows lesser filtration efficiency for the particle size between 0.3 to 0.7μ when compared to samples with SiO_2NPs incorporated. This factor remained same for membrane with chemical bond and spun bond fabric support.

Due to dipolar nature of the SiO_2NPs, the overall filtration efficiency of the samples increases when the concentration of SiO_2NPs increases in the polymer solution. However, while increasing the concentration of the SiO_2NPs, the pressure across membrane also increases and it is shown in Fig. 7. The chemical bond supported nonwoven membrane exhibited high-pressure drop value than the spun bonded support even with similar range of filtration efficiency. Due to the increase in diameter of nanofibres while increasing the SiO_2 concentration up to 30%, the pressure drop reduces.

Among the samples, sample S9 exhibits highest overall filtration efficiency with the pressure drop value of 6 mm in water where as with the chemical bond support, the result exhibits low efficiency with an increase in pressure drop.

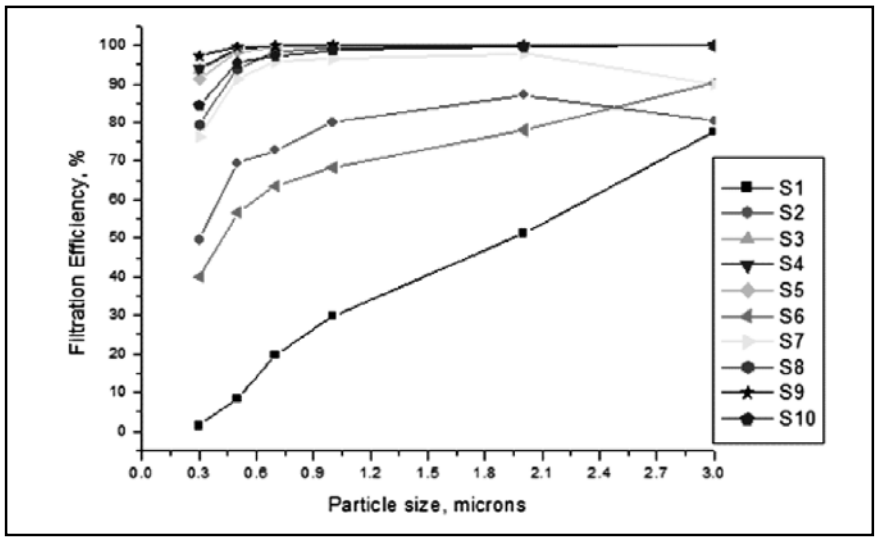

Fig. 6. Filtration efficiency with respect to particle size

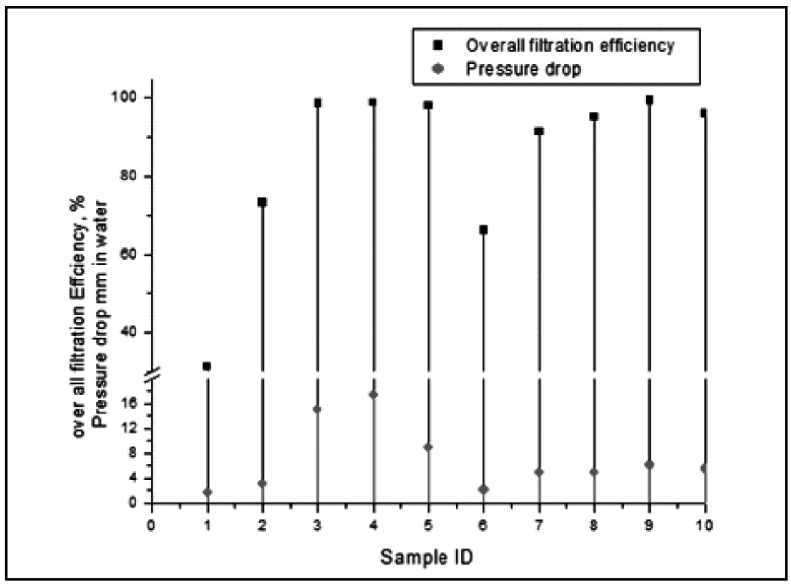

Fig. 7. Overall filtration efficiency and pressure drop

5. CONCLUSION

Nanofibre composite filtration membrane utilizing electrospun PAN nanofibres and SiO_2NPs sandwiched between nonwoven fabrics were successfully produced. Filtration efficiency of each membrane that is produced by using chemical bond and spun bonded support with electrospun core was analyzed. The composite media doped with SiO_2 displayed the best filtration properties, which is better than commercial filter media. The 20% SiO_2 incorporated membrane showed higher efficiency for both chemical and spun bond nonwoven support material. However, 20% SiO_2 incorporated membrane with spun bond composite showed maximum filtration efficiency than 20% SiO_2NPs incorporated membrane with chemical bond composite. Further increasing SiO_2 NPs there is a diminution of filtration efficiency due to agglomeration of SiO_2 NPs, which tend to increase the fibre diameter.

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Received: 04-09-2018

Accepted: 23-10-2018