

Industrial Scale Production of Nanofiber Overlaid Nonwoven

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1. Introduction

Electrospinning technology of nanofibers can be categorized into two methods: 1) conventional nozzle-based method, and 2) nozzle-free method. Nozzle-based electrospinning has a long history and nanofiber webs have been produced by this method. Elmarco, a Czech-based company, has developed a nanofiber production machine using a nozzle-free electrospinning method. Their system is based on free liquid surface electrospinning of nanofibers from a rotating drum surface.

We have developed a new nanofiber production system by nozzle-free electrospinning method that is not drum-based. The major advantage of our system is low capital cost because our method is simpler. Thus, low cost production of nanofibers for battery separator and high performance filter applications is now possible.



Fig. 1 PVA polymer jet generated from spinning unit (nozzle free)



Fig. 2 Pilot production line

Various manufacturing parameters have been tested on this line.

Target Substrate (Polyolefin nonwoven fabric) Polymer liquid jets

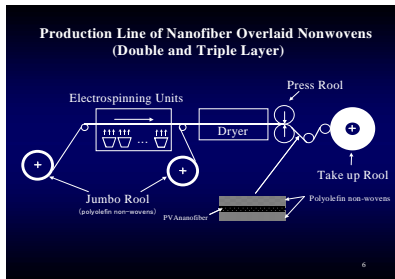


Fig. 3 Production process of PVA nanofiber overlaid nonwoven

Nanofiber is overlaid on the surface of polyolefin nonwoven for the improvement of handling property (two-layer structure). Additional layer of nonwoven can be added to the nanofiber side to make three-layered structure.

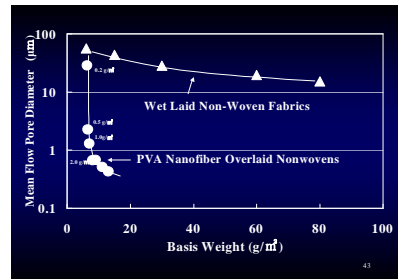


Fig. 4 Effect of basis weight to the polyolefin nonwoven and nanofiber overlaid nonwoven (two-layered) on mean flow pore diameter

Mean pore diameter of polyolefin nonwoven made of macrofibers (16µm in diameter) cannot be reduced smaller than 10µm by the increase of basis weight. Significant reduction of mean flow pore diameter to the submicron range can be achieved by overlaying small basis weight of

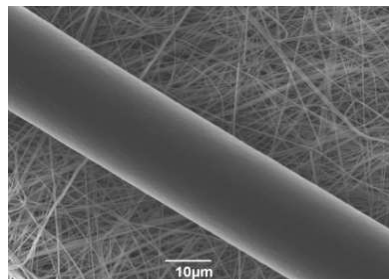


Fig. 5 SEM micrograph showing diameter difference of typical polyolefin fiber for wetlaid nonwoven (about 16 µm) and electrospun PVA nanofibers (about 200 nm)

Nanofiber overlaid nonwoven consists of these two different fibers of totally different sizes.

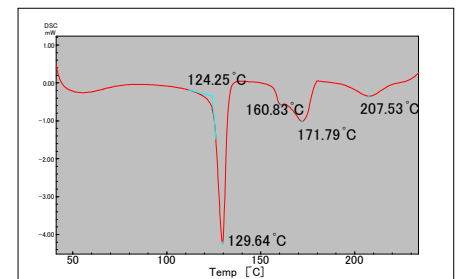


Fig. 6 DSC curve of nanofiber overlaid nonwoven consisting of PVA nanofiber and PE/PP sheath-core fiber

The curve shows heat adsorption peaks of PVA, PE and PP at 207.5 °C, 129.6 °C, and 171.7 °C, respectively.

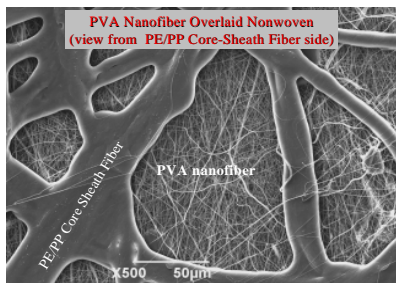


Fig. 7 SEM micrograph of nanofiber overlaid nonwoven (nonwoven layer side)

Large pores of wetlaid nonwoven is covered by nanofibers to achieve significant pore size reduction

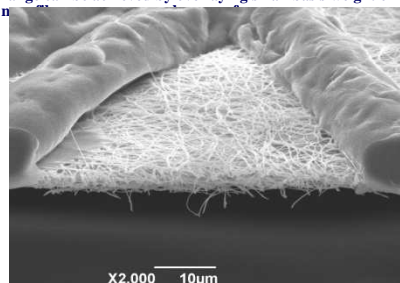


Fig. 8 SEM micrograph of nanofiber overlaid nonwoven (cross section)

Melted PE of PE/PP core sheath fiber penetrated into nanofiber web to form strong bonding. No damage is seen on the nanofiber web caused by the press roll

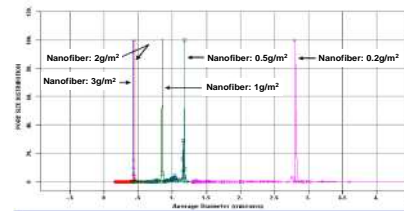


Fig. 9 Pore size distribution of nanofiber overlaid nonwoven

See extreme narrow pore size distribution

Characteristics of Nanofiber Overlaid Nonwovens											
Type	Composition	Substrate (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)	Wet Lay (g/m ²)
ZNCN	Layered (3-layered)	BD30	8.4	2.8	28	0.350	0.71	7	0.005	0.28	0.01
	Layered (2-layered)	BD30	4.1	1.4	15	0.375	0.75	7	0.005	0.28	0.01
	Layered (1-layered)	BD30	12.7	4.9	20	0.400	0.80	8	0.005	0.28	0.01
ZNCN	Layered (3-layered)	BD30	18.4	6.1	27	0.400	0.80	8	0.005	0.28	0.01
	Layered (2-layered)	BD30	12.7	4.9	20	0.400	0.80	8	0.005	0.28	0.01
	Layered (1-layered)	BD30	8.4	2.8	28	0.400	0.80	8	0.005	0.28	0.01

Table 1. Physical properties of nanofiber products including nanofiber overlaid nonwovens (two and three-layered products) and nanofiber web by itself. All of these products are available for sale and evaluation.

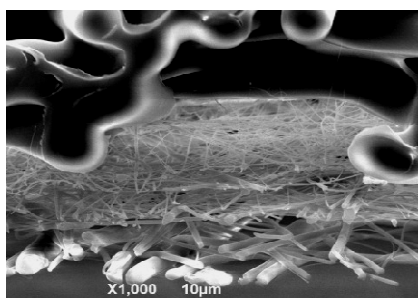


Fig. 10 Multi-nanofiber layered nonwoven Each layer consists of nanofibers with different fiber diameter.

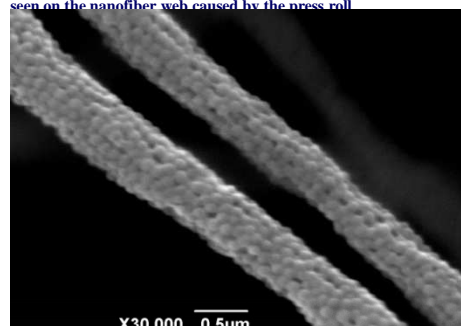


Fig. 11 PVA/SiO₂ composite nanofiber Nanofibers are coated by SiO₂ nanoparticles (100nm) on the surface. Significant improvement of heat resistance can be achieved

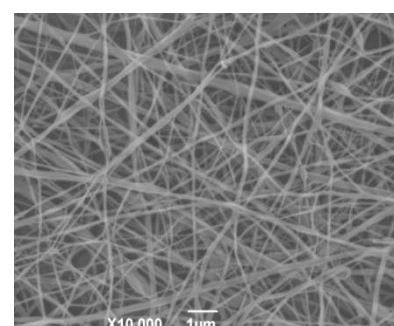


Fig. 12 Organic solvent based PVDF nanofiber

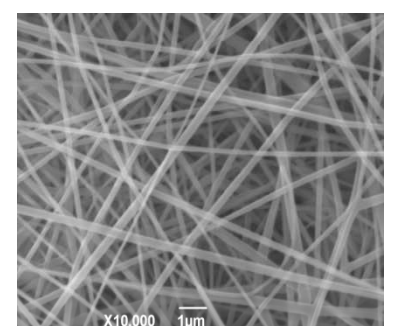


Fig. 13 Organic solvent based PAN nanofiber



Fig. 14 Development of Li-ion battery separators



Fig. 15 Production line of nanofiber overlaid nonwoven

Conclusions

- Hirose Paper has established industrial scale production of nanofibers by nozzle-free electrospinning technology.
- This innovative technology was combined with ultra-thin wetlaid nonwoven manufacturing technology of Hirose Paper and "Nanofiber Overlaid Nonwovens" was born.
- Combined layered structure of ultra-thin wetlaid nonwoven and nanofibers improved handling of nanofibers significantly without hindering superior properties of nanofibers.
- New development:
 Nanofiber /SiO₂ composite
 Multi-layered nanofiber nonwoven
 Organic solvent based nanofiber (PAN, PVDF, PI)
- Production line has been completed