RELATIVE SURFACE AREA OF NANOMATERIALS - - DREAM AND REALITY

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Abstract: *The nano fibrous assemblies (membranes) are extremely thin in the order of a few microns only. They have often relatively smaller porosity compared to micro fibrous membranes. Thus by considering their porosity as well as thickness, the nano fibrous membranes do not offer so huge real surface area as is evaluated from standard approach (surface area-to-volume or surface area-to-mass ratio) because the volume or mass are for nanofibrous materials too small. Rather the micro fibrous assemblies (membranes) provide sufficient real surface area of fibrous phase for end use applications e.g. filtration or surface activation. For estimation of relative surface area it is proposed to use surface area-to-macro surface ratio which is dimensionless and dependent on porosity as well as thickness. The advantages of this definition of relative surface area are demonstrated on the example of PA 6 nano and micro membranes.*

Keywords: *relative surface area, nano membranes, micro membranes.*

1 INTRODUCTION

The "nano" in nanotechnology comes from the Greek word "nanos" that means dwarf. One nanometer is one billionth i.e. 10^{-9} meter. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically changes when their size is reduced to the nanometer range. When a bulk material is divided into small size particles with one or more dimension (length, width, or thickness) in the nanometer range, the individual particles exhibit unexpected properties, different from those of the bulk material. The nanometer range is characterized by the transition of a material's behavior from "quantum like" behavior of atoms and molecules to the "continuum like" behavior of bulk materials [1, 2].

Often, nanomaterials are defined by a size range limited by at least one of the dimensions. This range may be 1–100 nm [3, 4] (British Standards Institution 2007; ISO 2008), 0.1–100 nm [7], less than 100 nm [5], or less than 500 nm [6]. The most common and accepted definition is probably the 1–100 nm range. In addition, it is sometimes suggested that to be counted as a nanomaterial the material must have properties different from those of the bulk form of the same chemical substance [7, 8]. The European Commission released their suggested definition of nanomaterials: "'Nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm" [9, 10].

The nanometer range is physically characterized by the transition of a material's behavior from "quantum like" behavior of atoms and molecules to the "continuum like" behavior of bulk materials. Especially for nano fibrous assemblies prepared by electrospinning is the mean fibrous elements thickness (diameter) is some hundreds of nanometers. But in general, all these fibers with a diameter below 1 μm (1000 nm) are often accepted as nanofibers [1].

One of the main advantages of nanomaterials is very huge relative surface area (surface area-to-volume ratio) [2]. This is in fact true for nanoparticles where are not limitations according to the macro geometry (unit volume).

It is widely published that by reducing fiber diameters down to the nanoscale, an enormous increase in specific surface area to the level of 1000 m^2/g or much more is possible. By reducing the fiber diameter from 10 μm to 10 nm, a million times increase in flexibility is expected. Recognizing the potential nano effect that will be created when fibers are reduced to the nanoscale, there has been an explosive growth in research efforts around the world. Specifically, the role of fiber size has been recognized in significant increase in surface area, bio-reactivity, electronic properties and mechanical properties. The enhanced reactivity and efficiency of nanofibers is based on the claim that nanofibrous membranes provide enormous availability of surface area per unit mass [3].

Limited thickness is serious limitation for volume of these objects calculation because the unit of their macro surface should be multiplied by real thickness and final macro volume is then very low. It leads to low amount of nanofibers and their low total surface area per unit of macro surface. Avoiding of this limitation leads to the unbelievable huge relative surface area values which cannot be achieved in real products. The same situation appeared when the properties as sorption capacity are calculated relatively to mass.

For estimation of relative surface area it is proposed to use surface area-to-macro surface ratio which is dimensionless and dependent of porosity as well as thickness. The advantages of this definition of relative surface area are demonstrated on the example of PA 6 nano and micro membranes.

2   NANOMATERIALS CHARACTERIZATION

Nanomaterials (nano fibrous assemblies) have some limitations for practical use because they are: too week and too sensitive to abrasion to be outer or inner part of clothing in conditions of wearing and maintenance, they have some effect on nano level only, they have low comfort (bad drape), and have serious limits for longer time use in common conditions. Their effects are often only temporarily.

There are often unprecise information oriented to highlight of „nano" from point of view of scientific content and to suppress weakness in real conditions. Instead of seriousness there are appeared „newspaper stories" oriented to dazzle of customers (nano layers with extremely thermal insulation, extremely surface area of nano layers, nano is equivalent to stronger, etc.). Of course, there are some big advantages of nano but the serious limitations as well.

It is well known that many properties of matters depend on the size range. In nano scale there are in some cases extra effect not following the bulk materials because the particle/wave nature of matter appears (quantum effects, tunneling, self-assembling). Nano objects are generally divided into three categories [3]:

1. Nanoparticles (3 ext. dimensions in the nanoscale)

2. Nanofibres (2 ext. dimensions in the nanoscale)

3. Nanoplates (1 ext. dimension in the nanoscale)

Plenty of characteristics are similar for all kind of nano object but simplest are derivations of relations for the case of nanoparticles. Their benefit is not limitations according to the magnitude of dimensions and therefore the properties or characteristics can be expressed in relative units (usually per unit of mass). Exclusive is relative mass expressed as density ρ where

$$\rho = m/V = m/(S\,h) \qquad (1)$$

Density is then ratio between particle mass m and particle volume V as product of particle cross section area S and thickness h.

In the case of nanofibers there are real limitations due to restricted cross section area and relative mass is better expressed as fineness T_T usually in tex units. It can be simply shown that

$$\rho = T_T/S \qquad (2)$$

Nanofibers are usually in the form of assemblies i.e. nanoplates.

In the case of nanoplates there are real limitations due to restricted thickness h only and better is to express relative mass as so called planar mass M_P usually in gsm (gram per square meter units) units. For this case it is:

$$\rho = M_P/h \qquad (3)$$

Nanoparticles (less 100 nm) contain 1 million atoms or less (spherical particle of 1 nm radius has approximately 25 atoms) and majority of atoms are on the surface. Nanoparticles are particles with at least one dimension smaller than 1 μm, and potentially as small as atomic and molecular length scales ~0.2 nm. Nanoparticles can have amorphous or crystalline form, and their surfaces can act as carriers for liquid droplets or gases. It is very simple to compute the geometrical changes due to use of particles with smaller dimension. Simple calculations are based on the ideal cubic particles with edge length D.

The specific surface area of cubic particle of edge length D and density ρ is defined by relation:

$$S_a = \frac{S}{\rho\,V} = \frac{6\,D^2}{\rho\,D^3} = \frac{6}{\rho\,D} \qquad (4)$$

The specific surface area is growing dramatically below particles of diameter 10 nm. Qualitatively similar trends are valid for related properties such as the ratio of surface/bulk atoms and the fraction of particle volume comprised by a surface layer of finite thickness.

Let the cubic particle of edge length D, with the surface area of $S = 6\,D^2$ is divided into n identical cubic particle of edge length d with total surface area $S_T = n\,6\,d^2$. Because the volume of bigger particle $V = D^3$ is the same as sum of volumes of n smaller particles $V = n\,V_S = n\,d^3$ the number of smaller particles is simply:

$$n = \left(\frac{D}{d}\right)^3 \qquad (5)$$

Relative gain of surface area S_R while maintaining the volumes is:

$$S_R = \frac{S_T - S}{S} = \left(\frac{D}{d} - 1\right) \qquad (6)$$

For example, if the particles of edge length 10 nm are produced from particle of edge length 10 mm, the number of particles is $n = 10^9$ and $S_R = 999$.

Increase of area S_n is then equal to:

$$S_n = S_T / S = D / d = \sqrt[3]{n} \qquad (7)$$

Typical length ratio $L = D/d$ for d equal to the atom size and D equal to particles size can be simply used for computation of:

1. Number of atoms in particle $n = L^3$

2. Particle mass $M_c = M_m L^3 / 6.022\,10^{23}$, where M_m is molecular mass of material.

3. Particle volume $Vp = 6\,d^2\,L^3$

Very common mistake is assumption that nano particles have better mechanical properties in comparison with more voluminous particles. In facts is cohesion energy per atom (size d) dependent on the size of particles (D) by relation:

$$E = E_b \left(1 - \frac{d}{D}\right) = E_b \left(1 - \frac{1}{L}\right) \qquad (8)$$

where E_b is cohesive energy for bulk material.

For nanoparticles it is ratio d/D from 0.1 till 0.01 and cohesive energy is increasing with particle diameter. It is interesting that starting from diameter of nanoparticles around 100 nm is E practically constant. This is one natural support of definition of nano range.

Many particle and molecular clusters properties (e.g. ionization energy, electron affinity, melting temperature and cohesive energy) show a smooth variation with size in the large particle regime. The following scaling laws can be applied for a general property (G) [5]:

$$G(N) = G(\infty) + a\,N^{-b} \qquad (9)$$

where N is size (number of atoms) in particle or cluster. Usually $b = 1/3$.

Large deviations (oscillations about the smooth trend) are observed for many properties in the medium and (especially) the small particle size regimes. Deviations arise due to quantum size effects (electronic shell closings) and surface effects (geometric shell closings).

Between particles generally occur gravitational and electromagnetic forces. Gravitational force is a function of mass and distance and is extraordinary weak between (low-mass) nano sized particles. Electromagnetic force on the other hand is a function of charge and distance. It is not affected by mass, so it can be very strong even when we have nano sized particles. The electromagnetic force between for example two protons is 10^{36} times stronger than the gravitational force. The stability in liquid continuous phase depends on the settling velocity v_s, which is proportional to their size squared $v_s \sim d_p^2$.

For nanoparticles is d_p very small and settling velocity is very small (sedimentation occurs after long time). For these particle sizes the diffusion is due to molecular collision i.e. Brownian motion [11-15].
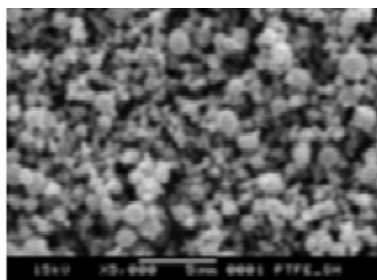
3 MEMBRANES CREATED IN ELECTRO-STATIC FIELDS

Traditionally high voltage electrostatic field is used for creation of nanofibrous assemblies and conditions of preparation are selected to avoid the creation of other structures (bead, solidified drops etc.). This technology, called electrospinning, is powerful in fabrication of two-dimensional (2D) or three-dimensional (3D) fibrous nanostructures [16, 17]. In fact the same technology can be used for creation of porous membranes based on electrospraying principle (deposition of droplets) or electronetting principle (see Figure 1).
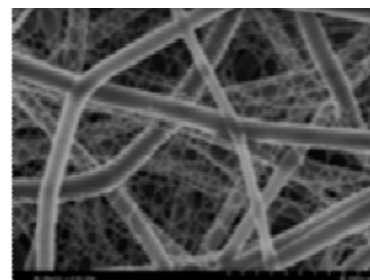
The structures shown in Figure 1 can be prepared by using the same machinery (needless electrospinning of Nanospider type) by changing of properties of spinning liquid phase, voltage and machine setting. All these parameters are critically dependent on the selected polymer solvent or dispersion chemical composition, physical form and concentration. These parameters are important for tuning porosity or compactness of membranes. The Nanospider electrodes which have been developed through last ten years of optimization can give big portfolio for electrospraying as well. The nano sized structures are deposited on supporting layer which can improve functionality.
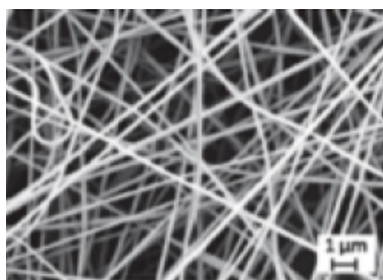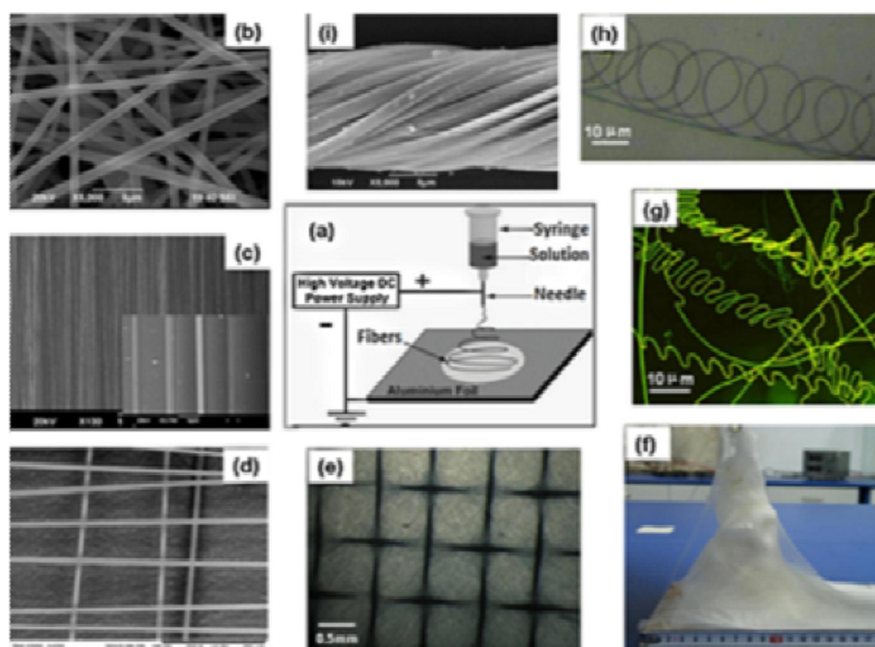

| Elspun nanofiber membrane | Electrosprayed PTFE | Electronetting effect |

**Figure 1** Porous layers prepared in electrostatic field

Figure 2 (a) Schematic diagram of electrospinning method, (b) electrospun polymer nanofiber mesh without orientation, (c) parallel and (d) crossed fiber array, (e) patterned fiber web, (f) 3D fibrous stack, (g) wavy and (h) helical fibers, and (i) twisted fiber yarns [18]

Electrospinning, an electrostatic fiber fabrication technique, is versatile and applicable in diverse fields. The nanoscale fibers are generated by the application of strong electric field on polymer solution, dispersion or melt [17]. The assembly of fibers produced by this process, offer various advantages like high surface area to volume ratio, changeable porosity and the ability to change composition to get desired function. Over the years, more than 200 polymers have been electrospun for various applications and the number is still increasing with time [17]. Electrospinning is superior in production and construction of ordered or more complex nanofibrous assemblies (see Figure 2).

The random orientation of fibrous mats fabricated by the conventional electrospinning may limit the potential applications, especially in the fields of electronics, photonics, photovoltaics and tissue engineering which need fast charge transfer or regular structures. To solve this problem, a variety of strategies have been proposed, such as pair electrodes collection, rotating drum or disk collection, auxiliary electric or magnetic electrospinning, double spinning, near-field electrospinning, direct-writing electrospinning, etc. Some approaches such as rotating drum collection have been used in the commercial electrospinning setup. The ability to consistently fabricate highly aligned fibers in large quantity over a large area is still a challenge [18].

Electrospraying utilizes electrical forces for liquid atomization [19]. Droplets obtained by this method are highly charged. The advantage of electrospraying is that the droplets can be extremely small (tens nanometers), and the charge and size of the droplets can be controlled to some extent by electrical means. Motion of the charged droplets can be controlled by electric field. The deposition efficiency of the charged spray on an object is usually higher than that for uncharged droplets. The membrane morphologies can be categorized into two main groups: dense and porous. The dense layer can be amorphous, crystalline (of different structures) or amorphous with incorporated particles (intrusions). The porous layer can be reticular, grainy, or fractal like. These structures are schematically shown in Figure 3. The membrane morphology depends, in general, on the temperature, the solvent used for spraying, voltage, physical properties of liquid phase (emulsion, dispersion, solution, density and surface tension), distance of collector from source, doping agents and the time of solvent evaporation. Post annealing and post treatment e.g. by plasma or microwaves can also modify the final morphology [20].
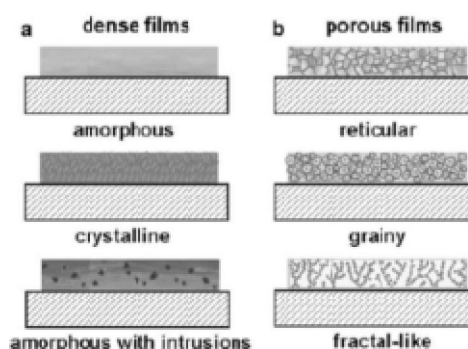
Figure 3 Typical morphologies obtained by electrospraying [20]

Electrospinning/netting or electronetting is a one-step strategy for fabricating nanofiber/net membranes comprising common electro spun nanofibers and two-dimensional (2D) soap bubble-like structured nano-nets [21]. Nano-nets, assembled from net-like structured nanowires with an ultrafine diameter (5-40 nm), exhibit several amazing characteristics, such as an extremely large specific surface area, high porosity and superior mechanical performance. The nano-net formation is connected with fast phase separation of the charged droplets [22].

4 RELATIVE SURFACE AREA OF MEMBRANES

Relative surface area of fibers is defined as surface area related to mass.

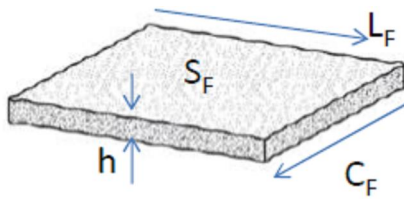The typical membrane (layer) shown in Figure 4 has length L_F, width C_F, and thickness h.

Figure 4 Membrane macroscopic dimensions

Corresponding macroscopic surface area is:

$$S_F = L_F \, C_F \tag{10}$$

Let this membrane is composed from N_v cylindrical fibers with length l, radius r and density ρ_F. The relative surface area SR [m^2/g] (surface area-to-mass ratio) is generally defined as:

$$S_r = \frac{2}{r \, \rho_F} \tag{11}$$

This relation is not dependent on the total fibrous assembly porosity P_o defined as:

$$P_o = 1 - \frac{w_T}{h \, \rho_F} \tag{12}$$

where w_T is planar mas (usually in gsm/1000, where gsm is grams of layer per surface area in meter squared).

The total surface area of fibers S_{FT} in membrane is simply expressed as:

$$S_{FT} = \frac{2(1-P_o) \, h \, S_F}{r} \tag{13}$$

In comparison with S_R is characteristic S_{FT} related to the thickness and overall porosity of membrane as well.

Much better characteristics of relative surface area is planar relative surface area (surface area-to-macro surface ratio) S_{SR} [-]. Quantity of S_{SR} is ratio of total surface area of fibers in layer S_{FT} and layer macroscopic surface area S_F:

$$S_{SR} = \frac{S_{FT}}{S_F} = \frac{2 \, (1-P_o) \, h}{r} \tag{14}$$

The S_{SR} is connected with S_R by relation:

$$S_{SR} = S_R \, (1-P_o) \, h \, \rho_F \tag{15}$$

The dimensionless quantity planar relative surface area S_{SR} is taking in account the porosity and thickness influence on the relative surface area of fibers in membrane.

5 COMPARISON OR RELATIVE SURFACE AREAS

PA 6 nanofibrous membrane (MN) with areal density of 1.3 g/m^2 was purchased from ELMARCO s. r. o Liberec. Spunbond PA 6 nonwoven fabrics (MM) with areal density of 100 g/m^2 was provided by Asahi KASEI Fibers Corporation. The morphologies of membranes were observed by Scanning Electron Microscopy (SEM) using a JEOL JSM-6510LV (Japan) with 10-20 kV of accelerating voltage. The membrane samples were coated with Au/Pd before being mounted on SEM chamber. The fibers on the membranes were randomly selected to measure the individual fiber diameters by identifying two points at opposite ends of a fiber diameter for each sample 50 times. The membrane samples were broken in liquid nitrogen and the cross section images were taken by SEM. Thickness was measured for each sample 10 times. More details about characterization and measurements of geometrical parameters of these membranes are given in [15]. Basic characteristics of both membranes are summarized in Table 1.

Table 1 Membranes characteristics

Characteristic	Micro membrane	Nano membrane
r [nm]	1520	140
h [mm]	0.53	0.00185
gsm [g /m^2]	100	1.3
P_O [-]	0.83	0.36
S_R [m^2/kg]	1196.2	12987.1
S_{SR} [-]	119.62	16.88

The calculated relative surface areas are given in Table 1. The ratio S_{SR} micro/nano = 7.0850 indicates that real relative area of micro membrane is much higher in comparison with nano membrane. On the other side the ratio S_R micro/nano = 0.0921, i.e. relative area per mass is for micro membrane very low in comparison with nano membrane due to differences in thickness mainly.

It is interesting that for nano membrane corresponds the mass 100 g to huge real surface area 77 m^2 but for micro membrane corresponds the mass 100 g to much smaller real surface area approx. 1 m^2. Very interesting is comparison of sorptive properties characteristics [6]. Under the same conditions was sorption of Acid Blue 41 by nano membrane

expressed as concentration 138 mg/g and by mico membrane 15 mg/g only. This leads to (wrong) decision about better sorptive properties of nano membranes. By using real sample sizes (membrane thickness) there was calculated concentration for nano membrane 0.017 mg/m^2 but for micro membrane much higher value 0.15 mg/m^2. From these concentrations are visible better sorption properties of micro membranes for real membranes thicknesses.

6 CONCLUSION

Definition of relative surface area S_R [m^2/g] as total surface area of fibers divided by their mass is not taking into account porosity P_o and thickness of layer h. Especially limitations due to extremely thin nano fibrous membranes in the order of a few microns only leads to over optimistic values of S_R. For the same real surface area of membranes is mass of nano membrane about two orders less in comparison with mass of micro membrane. Division of surface areas by their real mass then causes huge increase of nano membrane S_R in comparison of micro membrane S_R. By considering real thickness of both layers, the nano fibrous membranes do not offer so big real surface area as is evaluated from standard characteristic S_R (surface area-to-volume or surface area-to-mass ratio) because the real volume or mass are for nanofibrous materials too small.

For end use applications e.g. filtration, sorption or surface activation the micro fibrous layers are more beneficial providing sufficiently higher real surface area of fibrous phase.

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