ABSTRACT

AMID, HOOMAN. Hybrid Particle-Meltblown Nonwovens – Structure Property Relationships. (Under the direction of Dr. Benoît Mazé and Dr. Behnam Pourdeyhimi).

The ever-growing environmental need for cleaner air stresses the importance of filtration. Hybrid adsorptive filters and nonwovens are engineered to capture toxic gas molecules in applications like respirators and cabin air filters. Critical parameters for operation of air filters are adsorption capacity and pressure drop; these are determined by the type of adsorbent and the technology used to incorporate them, respectively.

One of the most popular hybridization techniques is the single-step coform process (i.e. intermixing and comingling of adsorbents with polymeric filaments as they exit the meltblowing die). Coform nonwovens with 10 – 99% mass concentration of adsorbents (activate carbon) and 0 – 13% particle shedding have been reported. Most of these structures go through post-processes such as adhesive lamination and/or heat bonding which are costly and result in covering a portion of the surface-pore area that is critical to adsorption capacity. In addition, effects of active feeding systems, microstructure, and process-structure-property relationships of these media have not been well investigated.

This study aims at developing guideline and a technology platform for fabricating high-loading, low-pressure-drop, non-shedding adsorptive nonwovens. In preparation of adsorption studies, a test apparatus for measuring dynamic adsorption for our model gas (NH$_3$) was developed and calibrated. In addition, different materials, such as HKUST metal organic framework and activated carbon, were evaluated as our model ammonia adsorbent. After selecting the model adsorbent particle, feasibility of its incorporation in single- and dual-beam meltblowing process using different configurations was investigated.

Unlike prior art, the feasibility of using passive gravity-fed systems and the impact of incorporation methods have not been successfully investigated until this study. Non-shedding hybrid media with 99% mass concentration of activated carbon are presented and their structure-property relationships are established. Particles were mechanically entrapped between the fibers to form stable multi-layered structures. These structures do not need post-processes or adhesives and their surface-pore area is not covered, and fully available for adsorption. In addition, the hybridization process did not adversely decrease the media air permeability.
Hybrid Particle-Meltblown Nonwovens – Structure Property Relationships

by
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DEDICATION

To my dedicated parents.
BIOGRAPHY

Hooman Amid was born and raised in Tehran, Iran. He completed his Bachelor's and Master's degrees in Textile Technology Engineering in Tehran Polytechnic (Amirkabir University of Technology), where he gained knowledge about surface functionalization and advanced textile structures for composite materials. He always looked for progress and the result of his search query to find the "top textile program in the world" led him to the College of Textiles at NC State University. He moved to Raleigh NC in July 2012 to pursue his doctorate degree at NCSU and joined The Nonwovens Institute in January 2013. He obtained the Graduate Certificate in Nonwovens Science and Technology in 2015 and will be obtaining his PhD in the summer of 2016. He is appreciative of what has been taught to him and is looking forward to creating value and giving this back to the community in the future.
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Last but not least, I owe many thanks to my love, Irene Wazgowska. You were always patient with me and are my true best friend. As things are getting more serious in the next month, I hope you always remain my best friend. Thank you for your supportiveness azizam.
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CHAPTER 1: Introduction – Overview of Filtration, Adsorption, and Adsorptive Filters
1.1 - FILTRATION PRINCIPLES
Removing the unwanted substances from gas or/and liquid bulk stream(s) by passing through filter equipment is defined as filtration. These substances include particles of different sizes or/and different unwanted/toxic gaseous or liquid molecules. To increase the durability and efficiency of a filter, filtration takes place in different stages, particulate removal and unwanted molecules removal [1, 2].

1.1.1 - Particle Collection Mechanisms
Figure 1.1 demonstrates the streamlines in the airflow, where different mechanisms of particle collection are depicted. Trapped particles act like extensions to the fiber and contribute to capturing/holding of the subsequent particles in the streamline.

![Particle collection mechanisms](image)

*Figure 1.1: Particle collection mechanisms [1]*

*Direct interception* happens when the size range of particle and obstacle, such as fiber, are comparable. The streamlines bend round the obstacles and carry the particle with them. The particle is taken to a distance less than half of its diameter from the fiber surface; therefore, it would hit the fiber on the flanks and stay put on there.

*Inertial impaction* happens for particles with higher kinetic energy, the ones that are travelling at high velocities or the ones that are large and heavy. Because of their high inertia,
these particles require high levels of energy to be carried by the streamlines; hence, they leave the streamline and hit the fiber (obstacle).

*Brownian diffusion* happens for particles with extremely small sizes that do not stick to the streamlines but meander about, in and across them. This diffusion behavior affects mainly small particles such as nanoparticles, and it is largely caused by the Brownian motion of the carrier fluid. Therefore, the small particle pops out of the streamline near the fiber surface, and sticks to the fiber.

*Electrostatic attraction* is another mechanism of particle collection that is relatively independent of the size scale or velocity of the particles. It technically occurs in the presence of charged particles and/or charged filter media [1, 3, 4].

### 1.1.2 - Filtration Mechanisms

A filter medium is a semi-permeable porous barrier with different thicknesses, actual filter areas, pore size (distribution), and densities. The target suspending particle in the bulk stream has its specific dimensionalities. Filtration mechanisms are defined based on pore size of filters and size of these target particles.

*Surface straining* occurs in filter barriers with smaller perforations compared to the diameter of the target particle. Rigid particles larger than medium pore size remain on the upstream surface. Perforated plates or a single layer of woven wires and/or plastic mesh of precise weaves are used for this purpose.

*Depth straining* happens for smaller/deformable particles that diffuse into the filter medium. These particles are trapped in distant pores from the medium surface or move through a pore until they reach a point where the pore is too small.

*Depth filtration* is another mechanism of particle capturing and is generally related to the adsorption of the particles in a bed of fibers. Fine particles move through a tortuous path in
the depth of the filter and irregular pores and are trapped on the pore surface by one of the aforementioned particle collection mechanisms, direct, inertial interception or diffusion. Practically, depth straining and depth filtration are done in the depth of the filter and have the same effects. Therefore, both mechanisms can be grouped together as one and under the title of depth filtration [1, 3, 4].

_Cake filtration_ takes place in the presence of high concentrations of solid in the suspension. As discussed before, the attracted particle can act as extensions to the fiber surface. The same concept happens on the surface of the filter when a layer of arrested particles bridges the pores and contributes to the filtration. Cake filtration happens on the surface of the filter and is a development of surface straining [1, 5].

### 1.1.3 - Filtration Characteristics and Parameters

Characteristics of a filter determine its properties/efficiency; they are categorized as follows:

*Smallest particle retained* defines the retention efficiency of a filter medium against particles of a standard test powder or aerosol. Table 1.1 shows the smallest particle retained for nonwoven filter media.

Table 1.1: Smallest particle retained for nonwoven filter media

<table>
<thead>
<tr>
<th>Media</th>
<th>Smallest particle retained (µm)</th>
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<tbody>
<tr>
<td>Dry-laid (felts)</td>
<td>10</td>
</tr>
<tr>
<td>Wet-laid (papers)</td>
<td>2</td>
</tr>
<tr>
<td>Wet-laid (sheets)</td>
<td>0.5</td>
</tr>
<tr>
<td>Polymer-laid</td>
<td>0.1</td>
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</table>

*Retention efficiency* versus particle size determines the efficiency of a filter at specific particle sizes. In general, retention efficiency of a filter is directly proportional to particle size. "Cut-off" point is the size at which the efficiency is < 100%. Since 100% efficiency is not typically achievable, another usual practice is to rate the medium at sizes where
efficiency is somewhat lower than 100%, such as 99.97%. Efficiency of a filter is graded (and only valid) at standard test conditions, these include nature/concentration of the particle, fluid properties, and filtration velocities. Parameters that influence the filtration efficiency include: a) filter media structure (pore size/shape/morphology), b) particle shape/size, and c) filtration mechanisms.

*Resistance to flow* (or pressure drop) is a major filter characteristic in industrial applications. This is defined based on upstream and downstream differential pressure and determines the energy (and cost) required to pass the fluid through the filter. Pressure drop is a function of media porosity (medium-dependent) and permeability (fluid-dependent).

*Dirt-holding capacity* (DHC) is an important performance characteristic that quantifies the amount of collected particle before exceeding a defined pressure drop. DHC depends on the type of the medium and filtration mechanisms by which particles are collected or trapped. Similar to filtration efficiency, DHC is measured/calculated at specific test conditions.

*Tendency to blind* (or clog) is important for reusable filters. A filter medium is considered blinded when the cleaning process fails to remove the residual solids and differential pressure increases. Fibrous filter media that are made from yarns or multifilament cloths are more prone to clogging [1, 3, 4].

### 1.2 - FUNDAMENTALS OF ADSORPTION

In general, adsorption takes place when a solid surface is exposed to a gas or liquid. The adsorption process is the enrichment of material or increase in the density of the fluid near an interface [6]. This enrichment process occurs because of the unsaturated and unbalanced molecular forces on the subject solid surface [7]. If the molecule (particle) is bound to the surface via weak Van der Waals forces, physical adsorption has occurred, which is a reversible process. However, if the attracted molecule (or particle) reacts and forms chemical
bonds with surface species of the solid, chemical adsorption takes place that is irreversible at constant conditions [8-10].

The extent of the interfacial area determines the overall increase of the adsorbed component. Hence, efficient adsorbents require large specific SA (surface area of unit mass of that material under stated conditions). Methods to determine the specific SA of a powder or porous material are governed by the adsorption measurements [6].

The adsorption process takes place in three steps, namely diffusion of the contaminant to the adsorbers' external surface, migration of contaminant molecules into micropores, and adhesion of the contaminant molecule to the surface of the adsorber [2, 6, 7, 11, 12].

Separation of gaseous contaminants in porous solids is achieved through steric, kinetic, or equilibrium effects. Steric effects take place in uniform aperture sizes through molecular sieving, whereas, the kinetic selectivity is a function of the rates at which adsorption and desorption take place. When the components of the gas mixture show little difference among their adsorbent and adsorption/desorption rates, equilibrium separation is the governing separation mechanism [13-16].

Adsorption occurs based on two types of forces, physical and chemical. Adsorption through physical forces (dipole moments, polarization, or dispersive forces) is called physisorption. Adsorption through chemical forces (valency) is called chemisorption [2, 6, 7, 11, 12].

1.2.1 - Physisorption
Physisorption is a reversible process that involves van der Waals interactions. The physisorbed molecule maintains its identity and goes back to its original form upon desorption. This non-specific phenomenon happens in multiple layers and resembles the vapor condensation process. Physisorption is an exothermic process with a relatively low enthalpy of adsorption (10 – 20 kJ mol\(^{-1}\)) [2, 6, 7, 11, 12].
1.2.2 - Chemisorption

Chemisorption is, generally, an irreversible process where adsorbed molecules chemically bond to (or react with) the adsorbent. Chemisorbed molecule, or the adsorbent surface group, loses its identity once in contact and cannot recover that upon desorption. Chemisorption depends on the reactivity of the adsorbent and adsorbate molecule, i.e. specific process that only happens at the surface of adsorbent (single layer). Chemisorption is associated with high enthalpy of adsorption (40 – 400 kJ mol\(^{-1}\)) and high temperatures favor the process [2, 6, 7, 11, 12].

1.2.3 - Adsorption Equilibria

When gas molecules strike the solid surface, some stick to the surface (adsorption) and some rebound (desorption). In the beginning of the process, the number of the molecules that hit the surface and stick to it is larger than the number of rebounding molecules. As time passes and surface becomes more covered, desorption rate increases and adsorption rate decreases. When desorption rate equals adsorption rate, equilibrium has been reached. Adsorption equilibrium can be approached in three ways: isotherms, isosteres, and isobars [7, 10].

An isostere is a plot of natural log of pressure versus the reciprocal of absolute temperature at constant amount of vapor adsorbed. Adsorption isostere is primarily used when the amount of target vapor is too high and continuous adsorption process cannot influence the concentration of the vapor in the bulk gas [11].

Isobars graph the amount of adsorbed vapor with respect to the temperature while pressure is constant. These graphs are very helpful in identifying physisorption versus chemisorption; this is due to the exothermic nature of physisorption.

Isotherms are the most common and useful representation of adsorption equilibrium data. They plot the adsorbent saturation capacity versus the adsorbate partial pressure at a constant temperature. Determination of adsorbent's SSA, pore volume, and pore size distribution is
usually achievable by isotherms [7, 11]. Isotherms are the basis for adsorption theories and for derivation of adsorption equations.

1.2.4 - Adsorption Theories

1.2.4.1 - Equations

Among the several adsorption isotherm equations that have been derived so far, the more important ones are Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller (BET), and Dubinin equations. When chemical bonding is the predominant adhesion force, Langmuir, Freundlich, and Temkin isotherm equations are very important. However, if van der Waals forces govern the adsorption process, e.g. physisorption of gases and vapors on porous carbons, BET and Dubinin equations are the most important isotherms. Yet, Langmuir and Freundlich isotherms are also important for describing physisorption [7, 11].

1.2.4.2 - Capillary Condensation

Based on this theory, apart from formation of multiple layers, the adsorbate gas/vapor can condense in small capillary pores of the adsorbent. This is a consequence of the lower vapor pressure caused by surface tension effects and the concave meniscus surface of the adsorbed layer.

Consider an adsorbent with a flat surface that is in contact with a gas and the pressure of gas is gradually increasing. When relative pressure is low and surface of adsorbent is not fully covered with the first adsorbed layer, the adsorption would be single-layer. After completion of the first layer, upon pressure increase, formation of second and subsequent layers commences, leading to multilayer adsorption. At this stage, liquidification (condensation) of the gaseous molecules takes place, a capillary condensation phenomenon. Since additional molecules are condensing on the formed liquid surface, the total amount of removed vapor/target gas molecules increases [7].
1.2.4.3 - Hysteresis

The lag between the adsorption and desorption isotherms is defined as adsorption hysteresis. Assuming a liquid in a capillary tube, when filling the tube, the vapor pressure is greater than when it is being emptied. The difference in vapor pressure is due to incomplete wetting that causes smaller liquid meniscus during the filling process than during the emptying process. Adsorption hysteresis helps calculate the pore size and pore size distribution [7].

1.2.5 - Parameters Influencing Adsorption

Temperature

In physisorption, adsorption rate would decrease upon increasing the temperature; there are two reasons for this. Firstly, as temperature increases, the adsorbate vapor pressure increases and the energy level of adsorbed molecules goes up. At this point, adsorbed molecules have the required energy to overcome the weak van der Waals forces and migrate back to gas phase. In addition, molecules that were already in the gas phase tend not to stick to the surface due to their high vapor pressure. On the other hand, as discussed before, the exothermicity of the physisorption results in a gradual release of heat during the process; this is approximately equal to the heat of condensation. The amount of released heat is not significant at low concentrations (below 1,000 ppm) and quickly dissipates through the bed's airflow; so it does not affect the process. However, at higher concentrations (e.g., 5,000 ppm), the accumulated heat in the bed can significantly increase the temperature of the surrounding environment. This leads to a considerable drop in adsorption and removal efficiency of adsorbent bed, resulting in organic vapor breakthrough.

In chemisorption, however, the rate of adsorption increases with increasing temperature. This is due to promoted rate of chemical reactions between the adsorbent and gas molecules [7, 11].
Gas relative pressure

The vapor partial pressure is proportional to total pressure of system and concentration of contaminants in the bulk gas. Generally, increasing the partial pressure of the vapor results in enhanced adsorption capacity. This increase is based on the decrease in the mean free path of vapor at higher relative pressures. Since the molecules are packed more tightly together, there will be a higher chance for each molecule to strike, hit, and adhere to available adsorption sites, leading to increased number of adsorbed molecules.

In addition, higher relative pressure corresponds to higher vapor concentration of in the bulk gas. The higher concentration acts as a force to promote the diffusion of contaminants to the surface of the adsorbent [7, 11].

Gas velocity

Concentration of contaminants (relative gas pressure) corresponds to hydrostatic vapor pressure in the bulk gas; but gas velocity corresponds to hydrodynamic pressure of the vapor. Gas velocity determines the contact or residence time between the contaminant stream and adsorber. Obviously, the longer the target contaminants reside surrounding the adsorber surface, the higher chance of capture. When the vapor stream is passing through the adsorbent bed more slowly, the probability of reaching to an available site is higher for the contaminants in gas stream. In most carbon-adsorption systems, if the velocity of the gas through the adsorbent is less than 30 m min\(^{-1}\), the capture efficiency will be 90% or more. However, to avoid some flow problems such as channeling, it is recommended to maintain lower limit of ~ 6 m min\(^{-1}\) for flow velocity [11, 17].

The cross-sectional area of the adsorber for a given volume of contaminant gas determines the velocity of the gas through the adsorber. Therefore, the minimum required cross-sectional area is specified based on the minimum velocity through the adsorber. In filtration applications, the cross-sectional area of media and flow rate are designed according to
allowable pressure drop for the system. Therefore, gas velocity is more important since there is a direct relationship between gas flow rate and pressure drop [7, 11].

_Humidity_

If humidity levels in exhaust gas streams are greater than 50%, installation of additional equipment is required to remove some of the moisture. Depending on the adsorption mechanism and type of the stream, different approaches are adopted to reduce/remove moisture. For instance, if adsorption efficiency is not affected adversely, humidity can be reduced by introducing heat to the contaminant stream. However, if the adsorption is physical and highly sensitive to temperature, adding additional adsorbent is a solution to offset the reduced efficiency. Moreover, for dilution systems that contain less moisture than the process stream, cooling the bulk gas can remove some of the water.

Vapor molecules in exhaust streams show strong attractions for each other rather than to the adsorbent. However, at high relative humidity (> 50%), the accumulated water molecules begin to compete with hydrocarbon molecules for active adsorption sites. Hence, the capacity and efficiency of adsorption system would be adversely impacted [7, 11].

_Bed depth_

The adsorption rate is a determining factor for design and calculation of bed depth. This is related to length of the mass transfer zone (MTZ) which dictates the minimum bed depth. It is necessary to provide a sufficient depth of adsorbent to have high removal efficiency due to the rates at which VOCs are adsorbed in the bed.

MTZ is the volume of the bed where mass transfer occurs at any one time, which starts on the gas inlet side of the media and moves through the bed. The breakthrough capacity is considerably diminished if the bed depth is not designed according to the required MTZ. Ineffective systems are consequences of wrong estimations of MTZ (or minimum bed depth) [7, 11]. MTZ length depends on six different parameters: (1) adsorbent particle size, (2) gas
velocity, (3) adsorbate concentration, (4) fluid properties of the gas stream, (5) temperature of the system, and (6) pressure of the system [11].

**Contaminants**

Contaminants are generally categorized into three main substances: (i) particulate matters; (ii) organic compounds with high boiling points; and (iii) entrained liquid droplets. The presence of any kind of contaminant in air stream can reduce adsorber's efficiency.

Dust or lint greater than three µm is considered as a particulate matter. Particulate matter would deposit on an adsorbent bed, and adversely affect the accessibility of organic compounds to a portion of adsorbent surface. These particles should be filtered in the first and second stages of filtration. Most physical adsorption systems are sensitive to particulate matters in the gas stream. In addition, when particulate matter concentrations are high, it is generally important to have pretreatment to have the most effective adsorption process. Most industrial adsorption systems are equipped with some type of particulate matter removal device to have longer service life.

High boiling point organic compounds, usually in excess of 260ºC, can also be contaminants for activated carbon systems. These are high molecular weight compounds that show a great affinity for carbon and their removal by standard desorption practices cannot be achieved easily. They can also form chemical reactions with the active carbon surface groups to form solids or polymerization products there are extremely difficult to desorb. Since the activity of active carbon is chemically lost, this is called chemical deactivation.

As discussed before, some operational problems are caused due to the presence of entrained liquid droplets. These droplets are non-adsorbing and can act the same as particulate matter and lead to deactivation or blinding of the bed by covering active surfaces. One of the operational problems that is particularly important for activated carbon systems are bed fires. This is caused by the release of high heats of adsorption if the organic liquid is the same as
the adsorbate. It is therefore necessary to employ an entrainment separator when liquid droplets are present [7, 11].

1.2.6 - Applications of Adsorption

Adsorptive media have a wide variety of applications in both liquid and gas phase. Some common applications are adsorptive gas capture, storage and separation, respiratory protection, and catalytic applications. To find the proper adsorbent for the target application, SA and pore characteristics, adsorbent-adsorbate interactions, and operating conditions are considered. For instance, in the case of separation and catalytic applications, the selectivity of the adsorbent is the key concept; this differs among the adsorbents [6, 9, 15, 16, 18, 19].

The most well-known adsorbent, activated carbons (ACs), can be used in water treatment/purification processes, recovery of precious particles, food industry, medical applications, biogas purification and catalysis, personal protection, and air treatment. In the gas phase, ACs have a broad range of applications from odor removal in air-conditioning systems to toxic gas purification in respirators (when functionalized) [1, 20].

During the past few years, MOFs (metal-organic frameworks) have had potential applications in a variety of industries due to their high selectivity towards different gases [15]. Many studies have been published on the applications of luminescent MOFs in biomedical imaging and drug delivery. They have afforded new opportunities in the field of gas purification/separation and catalysis, mainly, for gas storage applications. HKUST was challenged under realistic conditions in the EcoFuel Asia Tour in 2007, serving as a storage tank adsorbent for natural gas [16, 21]. In addition, many studies focus on the gas purification and toxic gas removal applications of MOFs [20, 22-25].

Application of ACs and MOFs in gas purification/filtration media include: odor and irritant/toxic vapor control in enclosed areas (vehicles, buildings, etc.), control of Volatile
Organic Compounds (VOC) emissions in industrial locations, and personal protective gears (clothing and face masks/respirators) [12, 16, 26].

1.3 - ADSORPTIVE FILTERS

After the brief introduction to filtration and adsorption, this chapter discusses the combination of the two. Adsorptive filter functionalities and media, popular adsorbents, and different fibrous nonwoven media are introduced.

Methods/techniques to incorporate adsorbents in nonwoven structures were reviewed extensively. A review paper titled "Hybrid Adsorbent Nonwoven Structures: Review of Current Technologies" was prepared; and has been published in the Journal of Material Science (chapter 2:) [27].

The section ends with discussions on state-of-the-art adsorptive filters, their limitations, related standards, and methods to evaluate them.

1.3.1 - Functionalities of Adsorptive Filters

Filtration is done in different stages within a filter unit. These stages may include separation of particulate matters (at different sizes) and separation of toxic/unwanted molecules from the bulk fluid. Removal/separation of toxic molecules is the main role/functionality of the adsorptive component in composite filter media.

Depending on the type of adsorption media, the filter may function as both particulate separator and toxic molecule separator. To achieve high efficiencies in adsorptive filters, ideally, particulate matters are removed from the fluid in preceding stages. This is due to the negative influence of contaminants on adsorption process. In some gas adsorptive media, adsorbents are embodied to reduce the moisture upstream before toxic adsorption takes place.
This is also due to the potential negative influence of moisture on adsorptive performance [7, 11].

1.3.2 - Adsorptive Filter Media

There are different types of adsorptive media for different applications; these are generally categorized based on the bulk fluid, i.e. gas and liquid. The major factors that determine the media type include fluid viscosity, amount of contaminant/pollutant, and process continuity [7, 11, 28].

Liquid filtration is a continuous/intermittent process that deals with fluids with different viscosities and contaminants/adsorbates that we may want to recover. Popular adsorptive filter media in most water filtration systems are fixed beds, expanded- and fluidized-bed reactors, adsorptive membranes, packed beds, and hybrid adsorptive nonwovens and foams. Fixed beds are used in large operation units; they consist of activated carbon granules (GAC) and function based on gravity. Expanded and fluidized-bed reactors are essentially improvements to the fixed bed, and there is emerging interest for them. Packed beds and adsorptive membranes/nonwovens/foams are used in smaller operation units. Packed beds are cartridges that contain GAC; whereas, adsorptive nonwovens are hybrid fibrous media that contain activated carbons (AC) embedded within their structure [26, 29-33].

Gas filtration is generally a continuous process that deals with air as the fluid (viscosity is not a big factor here). Recovery of the adsorbate may not be as important as it is in case of liquid filtration; however, pressure drop is a very critical process parameter in gas filtration. Popular gas adsorption filter media include huge AC adsorption (dryer) beds, AC cloths, packed beds, and hybrid adsorptive nonwovens. AC adsorption (dryer) beds are huge filtration units used in high purity and sterile compressed air systems; their maintenance/operation cost is so high. AC cloths are more effective than GAC and powdered AC (PAC) but are costly. Packed beds have a wide range of application in respiratory protection units; it is hard to achieve the proper balance between their AC loading, cartridge
size, and canister pressure drop. Hybrid adsorptive nonwovens have emerging applications in many smaller scale applications, such as respirators/facemasks, HVAC and vehicle cabin filters, etc. They offer flexible structures with low pressure drops and efficient filtration properties [1, 3, 4, 11, 12].

Therefore, the choice of adsorbent material(s) and fibrous nonwoven support(s) is application-driven. The target toxic/unwanted molecule(s) and the properties of bulk fluid stream determine the adsorbent material(s). The operational conditions/parameters determine the choice for nonwoven support. Regardless of the final application, the fibrous support should be able to contain the required amount of adsorbent component in a stable and effective fashion. The components of adsorptive nonwoven filters (adsorbents and nonwovens) are introduced and discussed in the next sections.

1.3.3 - Adsorbents
Adsorbents are bed(s) or layer(s) of highly porous solid materials or fine particles [6, 11, 34]. Due to their microporous structures, they generally exhibit large specific SA preferably ≥ 100 m² g⁻¹ in industrial cases [6, 18]. They are characterized and evaluated through adsorption isotherms, isosteres, and isobars.

Common types of porous adsorbent materials are activated carbons, followed by carbon molecular sieves, zeolites, activated alumina, and silica [35]. Some other kinds of adsorbents include pillared clays, synthetic polymers, aluminosilicate zeolites, zirconia, porous metal–organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) [6, 7, 11, 12, 14-16, 18, 36, 37]. The potential adsorbents that we considered in this study included ACs, MOFs and zirconia; their manufacturing, properties and applications are discussed below.
1.3.3.1 - Activated Carbons

Manufacturing: One of the most important industrial adsorbents is activated carbon (AC). ACs are manufactured from carbonaceous materials through two main routes. Regular ACs are produced in a two-step process, carbonization of the source material followed by heat treatment to extend their porosity (physical activation). Specialty ACs are produced in a single-stage process, impregnation of the source materials in a strong acid/base and carbonization (chemical activation).

Properties: ACs have highly developed porosities (micro, meso and macroporosity) and extended interparticulate SAs. They have a microcrystalline structure and in some industrial applications, their SA can be more than 1000 m² g⁻¹. Their pore structure is slit-shaped that is in contrast to the cylindrical porosity found in most inorganic adsorbents. ACs are available in three forms, namely Powdered Activated Carbon (PAC), Granulated Activated Carbons (GAC), and Activated Carbon Fibers (ACF). The size and structure of the ACs influence their pore characteristics, SSA, adsorption kinetics, regeneration, packing density and pressure drop of the adsorbent bed, handling, and immobilization. They are superior over most of the other adsorbents since they are inexpensive, hydrophobic and insensitive to moisture, thermally and chemically stable. In addition, their surface can be readily functionalized with different heteroatoms [6, 7, 9, 12, 14, 16, 18, 38].

Applications & limitations: ACs have important applications that generally involve adsorptive removal of color, odor, taste, and undesired organic/inorganic pollutants. These are used in different industries including food/beverage, pharmaceutical, medical, agricultural, fuel storage, air purification, (drinking) water/wastewater treatment, and chemical processing. ACs main limitations include effective adsorptive removal of specific organic/inorganic pollutants (such as reactive gases), fouling when exposed to low molecular weight impurities, early saturation in large units, and regeneration/disposal management [7, 12].
1.3.3.2 - Metal-Organic Frameworks

Manufacturing: Metal-Organic Frameworks (MOFs), or Porous Coordination Polymers (PCPs), were first introduced by Yaghi, Kitagawa, and their research groups [39-44]. They are generally produced by solvothermal synthesis of their precursor (metal salts and organic compounds); they form coordinatively-bonded three-dimensional porous structures. The common metal sources are zinc, aluminum, copper, nickel, iron, thorium, and uranium and the organic linker can be from simple molecules, such as terephthalic and formic acid, to very complex structures, like catenane linkers. Coordinative bonds interconnect their inorganic nodes (metal ions) and organic linkers to afford numerous kinds of different structures and properties. Different synthesis processes, such as hydrothermal, solvothermal, electrothermal, microwave assisted hydro/solvothermal, sonochemical, and mechanochemical, can yield MOFs structures. The most common MOF is HKUST (Cu$_3$(btc)$_2$(btc=1,3,5-benzenetricarboxylate), MOF-199, or Basolite C300)

Properties: MOFs are hybrid inorganic–organic coordination frameworks with infinite extended crystalline networks. These frameworks are highly designable and their framework, pore shape, pore size, and surface functionality can be easily modified. Compared to zeolites and ACs, MOFs have higher adsorption capacities, lower adsorption enthalpies, and lower thermal and mechanical stability. Their SSA is usually higher than 1000 m$^2$ g$^{-1}$ and they can adopt flexible structures with different SSAs.

Applications and limitations: Unlike ACs, MOFs have a wide range of potential applications in areas other than adsorptive removal of molecules. These include catalysis, biomedicines, ion exchange, gas storage and separation, sensing, biomedical imaging, and drug delivery. In gas adsorptive removal applications, these structures can be functionalized and designed to adsorb almost any target molecule. MOFs have not, as of yet, been deployed on a significant scale. One of reasons is the lack of enough metal/solvent sources to produce MOFs on a large scale. In addition, production time/yield is very inefficient and cannot keep up with the potential demand. High overall sensitivity of MOFs is the most important factor that decelerates their growth even on smaller scale. Although some MOFs have BET SSAs over
5000 m$^2$ g$^{-1}$, most of them exhibit a high affinity to water and moisture that limits their applications [15, 16, 37, 45-59].

1.3.3.3 - Zirconia

Manufacturing: Zirconia (zirconium dioxide) is a crystalline powder that is produced by calcination of zirconium compounds. The synthesis process is done via different routes, hydrothermal, solvothermal, sonication, and microwave irradiation. Since at high temperatures zirconia goes through disruptive phase changes, addition of small amounts of yttria is a common practice to eliminate this structural transformation.

Properties: Zirconia has a well-defined crystalline structure with high chemical purity. It offers high mechanical/chemical stability and has low production costs. Its designable size and structure, makes it affordable for zirconia to adopt an anisotropic fibrous structure. SSA of zirconia ranges from 10 – 320 m$^2$ g$^{-1}$.

Applications and limitations: Zirconia has been investigated extensively as the base stable sterilizable chromatography support in the field of protein purification [60-62]. Its main application is in ceramic production and protective coating. Special surface modifications are available to impart specific adsorptive properties towards specific gas molecules. Specific surface area of zirconia is very low and it does not have any microporosity (11 – 167 m$^2$ g$^{-1}$) [60, 63, 64]. In other words, physisorption by zirconia is very inefficient [60-65].

Broadly speaking, a promising adsorbent should possess high surface area, tailorable pore structure and pore size distribution, high adsorption capacity-selectivity, acceptable thermal-mechanical properties and hygrothermal stability, favorable adsorption kinetics and regenerability, as well as reasonable hydrodynamic flow resistance [15, 16, 66, 67].
1.3.4 - Nonwoven Media

As defined by EDANA (The European Disposables and Nonwovens Association), a nonwoven is "a manufactured sheet, web or batt of directionally or randomly orientated fibers, bonded by friction, and/or cohesion and/or adhesion" [68].

Nonwoven production methods are divided into three main categories of dry-laid, wet-laid, and polymer-laid [68, 69]. If the web requires extra strength, it goes through the bonding process. Bonding is done via different processes including chemical, mechanical, and thermal bonding. Chemical bonding uses binder materials, such as vinyl-based or acrylic-based polymers and natural starches, to bond the previously formed web. Mechanical bonding involves needlepunching, hydroentangling, and/or stitch bonding. Thermal bonding introduces heat to the web(s) and consolidates it [68].

1.3.4.1 - Dry-laid Nonwovens

Two main dry production techniques are carding and air-lay; they both use staple fibers and require some web bonding process. The carding process blends and opens staple fibers at first by means of different openers. They are then fed into the carding machine to form the fibrous web. Subsequently, according to the desired mechanical properties and final application, this web can be cross-lapped before the bonding process.

Air-laid webs are characterized by their high isotropicity and are often called random-laid web structures. After preparing the fibers, opening and individualization of fibers, they are uniformly dispersed in an airstream and deposited on a permeable screen/conveyor to form the web. The landing area is equipped with a suction system to ensure the formation of a continuous web that is bonded in the following steps [68, 69].
1.3.4.2 - Wet-laid Nonwovens

For a wet-laid structure to be considered as a nonwoven fabric but not a wet-laid paper, more than 50% of its fibers should have an aspect ratio (length to diameter ratio) of greater than 300. This is because the manufacturing technique/process for wet-laid nonwovens and (wet-laid) papers are very similar. Generally, a suspension of fiber/water is prepared, i.e. slurry. The slurry is deposited onto the web forming media, i.e. perforated cylinder or forming wire. Water drains out of the wire, fibers deposit on the forming media uniformly, and form the web structure. This web is bonded to gain the required strength [68, 69].

1.3.4.3 - Polymer-laid Nonwovens

The web is produced directly from the polymer resin in this single-step method. This is through the extrusion spinning of the molten or dissolved resin without any other intermediate steps. Two main techniques to produce such webs are spunbonding and meltblowing. These are both similar in principle but with distinct differences in processing configurations and final fabric properties.

In spunbonding, the extruded resin is firstly quenched and then attenuated to form a fibrous web with significant strength; this web may need bonding to gain the required strength and structural integrity. The filaments are drawn by the use of pressurized air and the process is capable of producing homo-, bi-, and multi-component filaments. Generally, high molecular weight resins with broad molecular weight distribution and medium to high melt viscosity are common polymers in spunbonding. The produced filament can be characterized by having high mechanical strength, low fineness and uniform fiber diameter.

Meltblowing process defers from spunbonding only in the sense that the extruded resin is firstly attenuated by hot pressurized air and then quenched. This distinct configuration yields a web that does not need further bonding; nonetheless, the fibers are considerably weaker than the spunbond fibers. Since the molten polymer is drawn first, the resin has lower molecular weight with narrower molecular weight distribution compared to spunbonding.
resins. In other words, resins used in meltblowing have relatively lower melt viscosity (or higher MFR). Meltblown fibers are characterized by having low mechanical strength, high degree of fineness, high surface area, and low fiber diameter uniformity [68, 69].

1.3.4.4 - High Surface Area Nonwovens

The total surface area of fibers is related to their fineness and cross-sectional shape. For materials with similar density, the less the denier (corresponds to higher fineness) is, the higher the surface area will be. However, in very fine-fiber structures, the compactness of the structure adversely influences the available pore volume [70]. Approaches to increase/enhance the surface area of fibers/nonwovens are divided in two general categories.

*Manipulating fibers cross-sectional shape*: changing the fibers cross section from round (most common) to deep-grooved or winged shapes would offer very larger surface areas. Winged-fiber nonwoven structures have less issue with compressibility compared to conventional round-fiber structures [71]. This was firstly introduced/patented by Fiber Innovation Technology, Inc (see Figure 1.2.a) and later improved/developed by Pourdeyhimi and coworkers (see Figure 1.2.b).

![Figure 1.2: (a) 4DG vs. round fibers and their compressibility [72], (b) winged fiber [73, 74]](image)

*Diameter reduction*: this is the simplest concept to enhance the surface area of fibers and there are three ways for this to be accomplished.
1) Spunbonded *islands-in-the-sea* (I/S) bicomponent webs: In this process, two polymers are co-extruded to form the bicomponent filaments. They are then fractured/fibrillated and bonded by mechanical and/or thermal means to form micro-denier fibers and nonwoven webs [75]. Fiber diameter of conventional spunbond webs (10 – 80 µm) can be reduced a lot in I/S webs (~ 0.5 µm) [76] (see Figure 1.3.a).

2) *Splittables* and *fibrillating* fibers: there are many bicomponent splittable fibers and the most common one is known as pie-wedge or segmented-pie. Evolon® is a splittable 16-segmented-pie endless bicomponent filament that is commercially available. Filaments are co-extruded and simultaneously split into microfilaments and entangled together with high-pressure water jets. These microfilaments are 30 to 100 times thinner than human hair [77] (see Figure 1.3.b).

3) *Electrospinning*: The most popular way to produce nanofibers with diameters of less than 100 nm is electrospinning, whereas, most meltblown fibers are limited to diameters greater than 500 nm [75, 78]. In general, the polymer solution is kept in a reservoir and subjected to a high electrical potential. As the electrostatic forces overcome the surface tension of polymer solution, the electrified solution starts stretching, bending, and forming a conic high-speed jet. This jet dries on its way to the collecting surface and forms a self-assembled nanofibrous web [79]. Electrospinning offers the opportunity to form hybrid structures (see Figure 1.3.c) that may also have a very high SSA and adsorptive functionality; this is discussed in Section 2.3.7 -.

Figure 1.3: (a) Typical I/S bicomponent filament cross-section [75], (b) segmented-pie [80], (c) cross sectional view of nanofiber web on spunbond substrate [81]
CHAPTER 2: Technologies to Manufacture Hybrid Adsorptive Nonwovens

This chapter is a manuscript entitled “Hybrid Adsorbent Nonwoven Structures: A Review of Current Technologies” by Hooman Amid, Benoît Mazé, Michael C. Flickinger, and Behnam Pourdeyhimi published in the Journal of Materials Science (2016), Vol. 51 (9), PP: 4173 - 4200, DOI: 10.1007/s10853-016-9741-x
2.1 - INTRODUCTION
The growing environmental awareness about the removal of pollutant gases from bulk gas streams is accelerating the investigation of adsorptive nonwoven filters. Adsorbents are bed(s) or layer(s) of highly porous solid materials or fine particles [6, 11, 34]. They generally exhibit large specific surface areas (SSA) that result from high micropore volume [6, 18]. Adsorbents' high SSA provides numerous sites for capture of toxic/unwanted molecules through adsorption process. Adsorption type determines the bonding energy between the molecules and surface, lower energy for physical adsorption and higher energy for chemical adsorption [8-10].

The most common types of porous adsorbent materials are activated carbons (AC), carbon nanotubes, carbon molecular sieves, activated alumina, pillared clays, silica gels, synthetic polymers, zeolites, aluminosilicate zeolites, zirconia, and metal–organic frameworks (MOFs) [6, 7, 11, 12, 14-16, 18, 36, 37]. Rigidity and anionic nature of aluminosilicate frameworks, high production costs, absence of homochirality, and functionalization difficulties are some of the limitations of traditional adsorbents. ACs are the most common adsorbents because of their reasonable price and commercial availability. MOFs are interesting to study because of their extraordinary high SSAs, versatile synthesis approaches, and functional tunability [7, 15, 16, 53, 82-86].

Applications of ACs and MOFs in gas purification-filtration include odor and irritant/toxic vapor control in enclosed areas (vehicles, buildings, etc.), control of Volatile Organic Compounds (VOC) emissions in industrial locations, and personal protective gears (clothing, face masks, and respirators) [12, 16, 26].

In practice, adsorbents are immobilized or entrapped within hybrid nonwoven structures [87] in two major forms: non-flexible packed beds [88], or flexible fibrous/polymeric substrates [26]. Packed beds offer high loadings of adsorbents but suffer from high pressure drops and non-flexibility. Fibrous nonwoven substrates, however, are flexible backbones for supporting or entrapping adsorbent materials. They offer unique properties such as engineered porosity
and pressure drop, versatility of the chemistry of base materials and production processes, and engineered chemical/physical functionalities [3, 28, 68, 69, 89].

Generally, adsorbents are immobilized within the nonwoven structure in three fashions: 1) there are physical bonds between adsorbent(s) and fibers, 2) adsorbents are mechanically entrapped within the structure, or 3) combination of both. The physical bond is achieved using some binder materials and/or thermal fusion of either of the components (adsorbents and fibers), causing a loss of SSA. In the case of mechanical entrapment, porosity of adsorbents remains unmasked; however, they are susceptible to shed out from the hybrid web [89].

Structures, properties, and applications of composite nonwovens are discussed in the literature [26, 90]. However, to our knowledge, there is no comprehensive critical review of how to incorporate adsorbents into nonwoven structures and how these methods compare to each other. Since each of these techniques will result in nonwovens with different properties, in the present review, we discussed and characterized them separately. The primary focus of this review is on hybridization techniques that incorporate ACs and/or MOFs in nonwoven structures, used in gas filtration.

2.2 - HYBRIDIZATION OBJECTIVES

Generally, using nanomaterials-polymer composite structures is a common practice to fix the nanomaterials and incorporate their properties into flexible polymeric structures. These properties include mechanical, thermal, optical, catalytic, wastewater filtration, gas transport and separation, etc. [91-106]. Polymer chains are often functionalized to efficiently embrace and immobilize target nanoparticles.

Because of the way they pack, adsorbents cannot be used as freestanding media without large pressure drops; hence, they need a support to contain them [1, 3]. Nonwoven structures can
contain the adsorbents and offer high filtration efficiencies and; this is especially true of electrospun, meltblown and spunbond structures [1, 3, 4, 7, 12, 16, 68, 69, 107].

The common aim of hybridization is to create a non-shedding composite medium with minimal covering (masking) of the adsorbents surface [89, 108]. Properties of these hybrid structures are application-driven; however, regardless of the application, three main design objectives are: i) immobilizing the adsorbents and tailoring the medium flexibility, ii) controlling the packing density of the medium, and iii) improving the filtration capacity of the final composite structure.

**2.2.1 - Immobilization and Flexibility Tailoring**

Immobilizing the adsorbent within the filter medium is critical. Many applications, such as water treatment and air/gas filtration, introduce a hydrodynamic feed stream to adsorbent materials. Due to the extremely minute size and low density of adsorbent particles, they can be swept away by the flow of the bulk stream. This phenomenon is known as dusting (or shedding). Pollutant particles face and hit the filter medium with different impact energies depending on their properties (size and relative density) and stream velocity [4]. In ultra-fine gas filtration applications, the nominal velocity within the media is between 0.3 to 3.5 m\(\text{min}^{-1}\). Considering the flow rate ranges for specific applications, 45,000 l\(\text{min}^{-1}\) for water filtration and 120 l\(\text{min}^{-1}\) for respirators, freestanding adsorbent particles are susceptible to dusting [1].

Beside the actual operational conditions, there are other reasons to immobilize adsorbents within the filter media. Filter media undergo some manufacturing and packaging processes that impose many mechanical and thermal stresses on the materials. Therefore, manufacturability and durability of the filter media require sufficient strength, resistance to corrosion and abrasion, flexibility, chemical and thermal stability, and elasticity. The latter, along with fatigue properties, are important in the case of expansion and swelling during the application. Expansions occur in pulsed and fluctuating flow rates and swelling happens in
polymeric supports in the presence of moist bulk gas stream [1, 4]. In addition, handling and reuse (regeneration of adsorbent) of such composite filters are easier when adsorbents are immobilized in the structure [109].

Media flexibility is another significant design parameter in filters. Packed-bed adsorptive media (adsorption columns and filter cartridges) contain adsorbents in rigid cages (or vessels constrained by the walls). These non-flexible structures cannot be implemented in filtration devices where flexibility is crucial to operation, such as facemasks [1]. Nonwoven substrates can provide not only a flexible mechanical support for the adsorbent component, but also a fibrous medium with particulate filtration functionalities [90].

2.2.2 - Controlled Packing Density

Among typical properties of a filter medium, pressure drop, filtration efficiency, and dust holding capacity are the most important properties reported in filter specifications. Pressure drop is critically important and is tailored according to the porosity and size (area and thickness) of the filtration unit. The proportion of voids to the overall volume of a material defines its porosity.

Pressure drop in hybrid adsorptive media depends on the porosities of its components (web and adsorber) and the distribution/packing of adsorbents within the structure. Adsorber’s porosity is inversely proportional to its hydrodynamic resistance (pressure drop) and mechanical strength [1]. High adsorption capacities in small filtration units, is achieved by employing adsorbents with higher microporosities or higher loadings of adsorbents; either of these options lead to higher pressure drop [1, 16]. Therefore, packing density of adsorbent materials is designed not only to meet the dimensional requirements of the unit but more importantly to reach a compromise between hydrodynamic resistance and filtration efficiency [1].
Packing density of adsorptive media is designed based on the requirements of target application. Gas storage devices ensure maximized storage capacity by adopting compacted adsorbent media. Filtration devices, however, require adsorbents to be uniformly dispersed through the media and to create the lowest pressure drop [16, 18]. In separation processes, binders are employed to increase the mechanical strength of medium and reduce pressure drop [15].

Nonwoven media are characterized by having low pressure drops (< 350 Pa) and highly porous structures (~ 90%) [1]. They can create filtration media with sufficient depths, affording designable dwelling time for contaminant molecules that adsorb at different rates. The depth of the filtration media should offer a compromise between the hydrodynamic flow resistance, adsorption rates, and desired filtration efficiency [1, 11]. For instance, spunbond-meltblown-spunbond (SMS) composite nonwovens can provide strong isotropic beds for adsorbent materials [76, 80, 110-112]. They can withstand high working pressures (~ 7 bars) and carry heavy loads of contaminant per unit area (~150 g m⁻²) [1, 92, 113].

Therefore, nonwovens provide the opportunity to create adsorptive structures with engineered packing densities and pressure drops. Tailoring the packing density of the adsorbents in filter media requires considering a number of factors. i) If water is present in hydrophilic polymeric housings, there will be a substantial increase in the backpressure resulting from swelling of the fibers [16]. ii) There is an optimum increase in the thickness above which the filtration efficiency would not increase [1]. iii) Bulk density and SSA of adsorbent materials is according to both volumetric and gravimetric capacities of the adsorber [114].

2.3 - HYBRIDIZATION TECHNIQUES
Although hybridizing the adsorbent materials with nonwoven beds would create an ideal adsorptive medium, the technique and mechanism by which the adsorbent is incorporated
and anchored in the structure is a matter of concern [115]. Based on their foundation, these techniques are categorized and reviewed critically below.

2.3.1 - Conventional Finishing/Coating/Padding Methods

2.3.1.1 - Implementation and Technology

Most of the techniques that fall in this category require the use of some kind of binding agent. Classical coating processes such as spray drying, foam coating, dip coating (dip and squeeze), and padding are useful immobilization techniques [16, 116-124]. Since particular specifications are meant to be imparted to the substrate, this technology can be referred to as a finishing process [16, 116, 117]. These conventional techniques are generally divided into two main subclasses of wet and dry particle insertion [16, 68, 116, 125].

In practice, wet particle insertion is accomplished in two manners. The first way is to mix the adsorbent particles with binder material(s), such as latex, and then fluid-coat the nonwoven substrate with the binder-adsorbent mixture. The second approach is to apply the binding agent onto the substrate and then introduce the adsorbent materials to the coated substrate. The coating can be applied by knives, rollers, bars, sprays, foam, or impregnation of the substrate in the binder bath [16, 26, 116, 126-130]. Different knife coating methods such as "knife-over-roll", "air knife", or "blanket knife" are employed. The coating dough can be a compound of powdered or granular activated carbon (PAC or GAC) and the binder polymer, such as polychloroprene. In this process, the ratio of AC to binder is constant and the mass of add-on is monitored [68, 131]. Next, the coated or impregnated substrate will be heated (air or irradiation) and cured [16, 116, 126].

Dry coating methods can be generally performed via calendering, melt coating, electrostatic spraying (2.3.8.3 -)Error! Reference source not found., or lamination (2.3.8.4 -). Calendering is the process where the target material(s) are spread on the substrate and the substrate is then passed through a set of heated calenders to fix the adsorbent materials onto the nonwoven fabric. Melt coating is done via inert powder coating (technically similar to
calendar). In extrusion coating, the target adsorbent layer is extruded and laid on the top of the substrate [26, 116, 132, 133].

Since some MOFs and ACs are conductive, Wie et al. (2008) proposed a sputter coating method for impregnating these materials into the nonwoven structures [16]. They sputter coated a PP spunbond nonwoven fabric with a nanolayer of copper. After washing and drying the substrate, copper deposition was accomplished by a Magnetron sputter coating system. They found that after increasing the coating thickness to 100 nm, nonwoven pore size and pore size distribution decreased. They hypothesized that it is possible to produce hybrid adsorptive nonwovens by coating the substrate with conductive MOF materials, which are intrinsically porous [134].

Another way to perform dry particle insertion is by airflow. Figure 2.1 demonstrates the schematic of this process [16, 135].

The particle insertion/penetration depth is due to the pressure gradient across the nonwoven substrate. Additionally, particles can be inserted by spraying, where there is no pressure gradient and particles retain their positions near the surface [16]. This can be accomplished by fluidized bed spray systems followed by substrate lamination in order to fix the particles and increase the particle retention of web (2.3.8.4 -) [135].
Alternatively, to decrease the differential pressure, some commercial filters are manufactured by coating open-pored polyurethane with PAC and GAC. This is done by impregnating polyurethane foam in a slurry of latex binder and AC [135, 136]. The thickness of the media can be between 2.0 to 30.0 mm [137].

In another study, electrospun nylon 6,6 was placed directly on the top of a porous AC-loaded polyurethane foam. The electrospun coating was supposed to eliminate the penetration of aerosol particles through the foam layer by taking advantage of minuscule porous structure of the electrospun web [138]. Figure 2.2 shows the structure of these two membranes separately.

![Figure 2.2: (a) Porous polyurethane foam containing AC (scale bar: 200 µm); (b) electrospun nylon 6,6 nanofiber coating sprayed onto surface of the foam (scale bar: 2 µm). Reprinted from [138] with permission from Elsevier](image)

### 2.3.1.2 - Characteristics and Considerations

In wet coating processes, the nature of the solvent and transportation media are important. Not only do these media need to be compatible with both adsorbent materials and nonwoven bed, but also they need to meet the requirements of the final product. Some issues in this regard include biodegradability and non-toxicity of the solvent system, mass transport properties, chemical effects on the adsorbents, avoiding particle agglomeration, and ease of reusing and regeneration of the solvent [16]. The major problem of this method is the blockage of adsorbent surface and diminished surface area functionality and adsorption...
capacity [117, 139, 140]. Using granular adsorbents is advantageous over their powdered counterparts since the coating process covers a smaller portion of the adsorbent and the larger portion of the surface will remain uncovered and functional [141]. Additionally, the penetration depth and stability of the particles within the structure are critical, especially in the case of foam coating [16, 116]. The energy cost of wet particle insertion is mainly associated with moving the solvent/water around and curing/drying the coated substrate [16].

In dry particle insertion methods, namely gradient-pressure airflow and spray methods, parameters of interest include (1) particle mechanical stability; (2) physical properties of particles (e.g., size, shape, hydrophobicity, hydrophilicity); (3) properties of nonwoven materials (e.g., mass, density, water and/or air permeability, pore size); (4) particle energy during the penetration process; and (5) particle acceleration before the dissipation of required kinetic energy [16]. Therefore, the optimal relationship between particle size, substrate pore size, and particles kinetic energy are necessary factors to prevent structural disintegration of the substrate.

Calendering process requires adsorbent materials to have sufficient mechanical stability to withstand the calenders nip pressure and maintain their structural integrity [16, 116]. In addition, both calendering and melt coating would lead to partial blockage of adsorbents’ pores and reduced functionality [16, 140].

Sputter coating methods are more expensive with lower deposition rates compared to other coating/finishing methods. Although particles are dispersed more uniformly in sputter coating [116], stability of nanoparticles in substrate raises a major concern for application of these structures in filtration [16, 116].

In general, coating methods are inexpensive and commercially developed/available. This is opposite to some other techniques (2.3.5 - and 2.3.7 - that are not widely examined and still need further study.
Wet coating processes induce partial blockage of pores and reduced functionality of adsorbent materials, true about some other hybridization techniques (2.3.2 - 2.3.3 - 2.3.6 -). Compared to other techniques, solvent/water system that is used for applying adsorbent materials raises some environmental issues (also true about wetlay technique 2.3.4 -) and additional energy/cost issues.

Among the methods in this category, the airflow method maintains the functionality and structural integrity of adsorbent materials and can be performed in-line with the nonwoven production. Nonetheless, there is no physical bonding between adsorbents and nonwoven media, so the media is vulnerable to dusting. This is also the case in wetlay process (2.3.4 -)

2.3.2 - Compounding Adsorbent Materials with Base Polymer

2.3.2.1 - Implementation and Technology

Functional nanoparticles of interest, PAC/GAC and/or MOFs in this case, can be added to the polymeric support material or resin in the meltspinning/meltblowing process. The mixed melt is extruded in the form of filaments/nonwovens [142-145]. Besides meltspinning, the prepared adsorbent-containing mixture can pass through a coagulation bath to form filaments from which nonwoven substrates will be produced [105, 117, 146, 147]. Carbon nanotubes can be compounded with the polymer solution in the coagulation bath to enhance the mechanical properties [99]. Such immobilization and hybridization techniques are common practice for the wastewater treatment (copper removal) where PAC is mixed with hydrophilic polyurethane liquid prior to the foam formation [109].

2.3.2.2 - Characteristics and Considerations

Meltblowing compounded resins and properties of resulting products are influenced by the following factors: particle weight %, particle uniform dispersion, molecular weight of the
molten polymer, particle properties (dimensions, shape, and density), and processing parameters (screw configuration, number of screws, temperature profile, etc.) [147-150].

Polymer-particle melt compound undergoes huge rheological changes. The most significant rheological parameter is melt viscosity (or melt flow index) that determines the spinnability of the polymer. Melt viscosity of the compound depends on original polymer properties, polymer-particle interactions, and weight percentage (concentration) of the added functional particles [149-152].

The most important limitation to this technique is the loading amount of adsorbent materials in molten resin mixture. This is due to the profound effect of compounding on shear rate and extensional viscosity of the melt [94, 153-155]. In addition, depending on the production speeds and shear rates, the compounded melt shows different rheological properties and shear viscosity behaviors [154, 155]. This complex behavior of compounded melt at high particle concentrations is a major impediment for meltblowing, a fast single-step nonwoven web formation process [156-159]. High concentrations of added material in visco-elastic polymers can have the following negative effects: 1) low and non-processable melt flow index (high melt viscosity), 2) reduced melt elasticity and resulting die swell phenomenon, 3) likelihood of particle agglomeration, 4) diminished moldability, and 5) induced polymer degradation (based on polymer-particle chemical compatibility and interfacial surface chemistry). There is no specific range for this concentration since each polymer-particle system would behave differently [150-152, 160, 161]. Adding compatible surfactants [147-149], using end-functionalized polymers [162], and using ultrasonic particle dispersion can help reduce the particle agglomeration [150].

The other limitation/consideration is the dimensions of target adsorbent particles relative to fiber diameter. This is important as the functionality of adsorbent (accessible surface area and pore) depends on how it is attached to the fiber; i.e. contained in the fiber structure or point-attached on the fiber surface. It is reported that the radial placement of particles relative to
fiber axis depends on particle size. Larger particles tend to cluster on fiber surface and smaller particles agglomerate in the center of fiber [163-165].

Since particles are partially bonded to the fibers/web, the filter media do not suffer from dusting as much as wetlaid (2.3.4 -) or coform (2.3.6 -) hybrid structures [117, 148]. For the same reason, the filter media will have a uniform 3-D distribution of the adsorbent component. This method is environmentally benign since no solvent system is involved in the production [110, 149, 166]. However, this hybridization method will potentially block the adsorbent materials’ pores and adversely influence the mechanical properties of fibers and nonwoven fabrics.

2.3.3 - Thermal Bonding of Adsorbent to Substrate

2.3.3.1 - Implementation and Technology

In general, this method refers to all techniques by which either the nonwoven substrate or the adsorbent material is heated to make bonds at points of contact between the two. The nonwoven fabric is produced by different methods, such as dry-laying, wet-laying, spunbonding, or meltblowing [167].

Approaches to introduce heated adsorbent component to nonwoven fabric include: 1) spraying an air stream containing the heated solid particles onto the substrate; 2) dropping or sprinkling the heated solid particles onto the substrate; 3) passing the substrate through a shaking reservoir/chamber containing heated particles; 4) immersing and passing the fibrous sheet through the heated particles; and 5) exposing the substrate to a fluidized bed stream of heated particles [152, 167, 168].

When heating the substrate, adsorbent materials can be sprinkled over the nonwoven fabric in the first step and then the coated layer enters a heating zone. In this way, softening or partial melting of the nonwoven fabric occurs and particles will bond to the fibrous structure [2, 116]. The fibrous support can be electrostatically charged before entering the particle-
dispensing zone. This will enhance the deposition ratio by the added contribution of electrostatic deposition to the normal gravitational deposition [2] (2.3.8.3). Figure 2.3 shows the complete configuration of such a device.

![Figure 2.3: Device for manufacturing carbon-powdered nonwoven fabrics](image)

Heating through radiation is advantageous when using dark adsorbent particles, such as AC. In addition, the blower fan stabilizes the deposited sunk particles on the structure [2].

Commercially available particle-coated filters are AC air filter media from Permatron®. Polyester nonwoven substrates are impregnated with finely ground coatings, and subsequently heat-set so that the coatings will be retained in the filter media even when the media is rinsed or vacuumed. Filter media thickness ranges between 0.47 mm to 1.27 mm that is mostly composed of GAC [169].

Alternatively, nonwoven substrate is made of bicomponent sheath/core fibers (BiCo) [170, 171] and adsorbent particles (or ACF [172]) are heat-bonded to the sheath component [16,
Bicomponent nonwoven structures, webs comprised of two fiber types, are also reported to be useful in this regard [178]. The fibrous structure is comprised of high-melting-temperature fibers, as the support, and low-melting-temperature fibers into which adsorbent component fuses upon heating the substrate [179]. In this method, adsorbent materials are applied on the substrate by some means, such as spraying, and the web is subsequently heat-treated. Upon heating the web (or particles), the sheath component softens and particles adhere to surface of the fiber [16, 173]. The same concept occurs for low-melting-temperature fibers in bicomponent nonwoven structures [116, 180].

### 2.3.3.2 - Characteristics and Considerations

Control parameters for thermally bonded hybrid nonwovens include the temperature, relative density, kinetic energy, heat capacity, and size of the heated particles. Melting temperature and weight percentage of sheath and core polymers, air permeability, and pore size distribution of the nonwoven fabric are other determining factors of the process [167, 168, 173].

If the temperature of air stream, containing the heated particles, is more than 200°C higher than the melting temperature of nonwoven fabric (or core component of sheath/core fibers), there will be an undesirable shrinkage in the web. In case of single component nonwoven webs and such high temperature gradients, there might be broken threads rather than just shrinkage [152, 167, 168, 173]. In such high temperatures, the heat stability of the adsorbent component is also important [117]. The dwell time or travel rate of substrate is adjusted according to the amount and type of adsorbent particles, and the nonwoven fabric properties (material, web thickness, and basic weight) [2]. Generally, it is preferable to maintain the temperature of particles 80°C - 100°C above the melting temperature of the fibers, and to have the core-component weight percentage of more than 90% [152, 167, 168, 173].

To avoid dusting, functional particles should have an average size of equal to or less than \( \frac{1}{3} \) of the average diameter of the fiber [152, 167, 168].
Substrate's pore size distribution and adsorbent's relative size determine uniform distribution of particles in final structure include [152, 167, 168]. In terms of loading, it is preferable for the polymeric component to be about 10-25 wt % of a particle-loaded web [173].

The main disadvantage of heat-bonding technique is the partial blockage of adsorbents' pores. Many functional particles would be excessively buried in fibers and less than 50% of total surface area would be effectively available [152, 167, 168, 173]. Another drawback of this method is the high energy required to heat-treat (or subsequently calendar [168]) the substrate [16]. In addition, these particles are susceptible to abrasive removal if the filter medium is subject to high processing/operation stresses [173].

In general, heat bonding of adsorbent materials would be an effective hybridization technique when production time and environmental issues are matters of concern.

2.3.4 - Incorporation of Adsorbent Materials in the Wetlay Process

2.3.4.1 - Implementation and Technology

Activated carbon fibers and particles can be incorporated in nonwoven beds via wetlay process to produce Chemical Protective Clothing (CMC) and filtration media [3, 177, 181-184]. Nonwoven substrate is the supporting bed for the AC constituent that serves to adsorb dangerous chemicals and toxic vapors.

The AC constituent is mixed with the wetlay fiber slurry to yield a single-layer hybrid wetlay structure [3, 181, 183, 184]. Generally, there are three steps to produce such media; a) a suspension of staple fibers (usually cellulosic fibers such as pulp) and adsorbent component is prepared; b) the aqueous suspension is deposited onto a papermaking-forming perforated surface; and finally c) water is removed via vacuuming to yield the hybrid fibrous medium [78, 140, 185, 186].

Industrially, these structures are made for filtration/prefiltration [184, 187] where three layers of wetlay nonwovens, with the middle one or all containing the carbon constituent, are
laminated into a single pleated filter [188]. FACT® filtration media are commercially available from KX Technologies where adsorbent particles are immobilized by non-cellulosic fibrillated nanofibers [189]. The adsorbent component is immobilized within wetlay nonwoven structures using fibrillated fibers, such as fibrillated acrylic fibers [3, 183, 190-193]. In general, AC particles or fibers are suspended in the slurry containing acrylic fibrillated fibers; subsequently, the suspension is wet-laid using conventional papermaking process [3, 183, 190-194].

Fibrillation of fibers is done by high speed shearing of fibers at temperatures greater than 30°C; enzymes may be employed to accelerate the fibrillation process [183, 191-193]. Wet-end additives, fluctuating agents, and surface-active agents can facilitate the web formation process [183, 190-193, 195]. Chemical post-treatments are available to impart different functionalities and properties such as abrasion resistance, toughness, or improved adsorption [185].

2.3.4.2 - Characteristics and Considerations

Hybrid wet-laid adsorptive media have medium-to-high production costs. They are characterized by having improved sheet flexibility, high sorptive characteristics, high porosity to fluid flow, processing speeds normally associated with papermaking processes, and a wide range of applications from military uniforms to gas separation media [78, 192].

To modify the mechanical and/or physical properties of final product (such as higher mechanical strength or operational temperature), short glass fibers or other synthetic fibers can be added to the slurry [194, 195]. The use of active agents, with controlled weight percentage and size, promotes uniform 3-D distribution of adsorbent materials within the web structure [183, 185, 189, 193]. It is recommended not to use chemically functionalized particles as the nature of the aqueous process could render chemically-unstable adsorbent materials inoperative [140].
Wet-laid nonwoven media are capable of uniform immobilization of adsorbent particles sized 1 to 80 microns. Preferably, the weight percentage of particles smaller than 10 microns should not exceed 15% of the total composite medium weight [189-192]. When using fibrillated fibers, more adsorbent particles can be immobilized; this is due to mechanical interlocking action of fibrillated fibers [190-192, 194]. However, denser structures are associated with higher pressure drops [116, 140].

Common fiber size used in a wetlay process is about 0.7 – 8 denier (10 – 35 microns in diameter) with lengths ranging 5 – 36 mm [185]. However, if employing fibrillated fibers, the fibrillated fibers should be less than a micron in diameter, preferably from 50 – 400 nm, and 1 – 25 mm long [183, 189, 193]. Weight percentage of fibrillated fibers should be 10 – 20% of the final composite structure [185, 190-192]. To improve the performance, ACF with lengths ranging 5 – 10 mm can be added to the slurry in weight percentages similar to that of AC particles.

The most competitive advantage of the wetlay process is the absence of adhesives or melt fusing compared to the previous techniques, resulting in not-shielded pore structure of the adsorbents [188, 194]. Production time tends to be as short as that of papermaking processes and the absence of various chemicals promotes the environmental issues [78]. However, following disadvantages are associated with this process:

(a) The energy price is high since water is being moved around in the whole system [68, 69];

(b) There is no actual physical or chemical binding between the web and adsorbents, so the structure is vulnerable to dusting [116]; and

(c) The process is not compatible with most of MOF materials because of their hydro-sensitivity and hydro-degradability [196-202].
2.3.5 - Direct Growth on the Substrate

2.3.5.1 - Implementation and Technology

In general, this method involves the synthesis of MOFs in the presence of final substrate that is usually pre-functionalized. Two general approaches are in-situ growth and secondary or seeded (also called layer-by-layer [203]) growth. The in-situ growth refers to immersion of pre-functionalized substrate in the growth solution. However, in the seeded growth method, the substrate already has the preattached seed crystals when immersed in the growth solution [204-207]. The latter stepwise formation method is popular for preparation of mixed-ligand or pillared-layered MOF materials. The seeded growth method is used for zeolite membranes and yields highly oriented growth on the substrate [208]. Modifications of the substrate prior to growth process results in improved heterogeneous nucleation of MOFs and stronger interfacial bonding between the native substrate and MOFs [205, 207, 209, 210].

Among the non-polymeric support materials, the most commonly-used are α-alumina [203, 205, 209-213], TiO₂ [205], silica, porous alumina, graphite [203, 214], zeolites, carbon [214], and porous potassium hexatitanate disks [213]. Although these inorganic membranes are rather solvent-insensitive, thermally stable, and selective, they suffer from low flexibility/breathability, brittleness, and thermal expansion [214, 215]. Polymeric nonwoven substrates, however, offer greater flexibility [203, 214] and breathability. This makes nonwovens a great option for protective clothing, filtration and gas separation applications [216, 217]. MOFs have a great potential of anchoring and growing directly on polymeric substrates [205] due to their organic-inorganic hybrid nature. Fibers that have been used as the support for direct growth of MOFs include silk [203], cellulose [207, 218], polyester and wool [216]. Polymeric membrane supports include polymethylmethaacylate, polyimides, Matrimids®, and polysulfone [214].

Centrone et al. (2010) synthesized MIL-47 directly on electrospun polyacrylonitrile (PAN) substrates via microwave irradiation. PAN solution was electrospun, collected on an aluminum foil, and folded and heat-pressed for enhanced mechanical strength. The substrate was then placed in a vial that contained the precursor solution of MIL-47 to be irradiated in a
microwave for 5 seconds to 30 minutes. Finally, the MOF-coated PAN substrate was removed from the solution, rinsed and dried for characterization. The produced substrate was found to be a proper medium for filtration applications [50].

Pinto et al. (2013) reported the attachment of HKUST-1 to PAN electrospun nanofibers (see 2.3.7 -). The electrospun PAN substrate was firstly reacted with copper acetate for two hours and then the BTC solution was added drop-wise to the reaction solution for the in-situ growth [219].

Fan et al. (2012) prepared a macroporous SiO$_2$ wafer with a thickness of 2 mm as the supporting scaffold for ZIF-8/PVP (Polyvinylpyrrolidone) composite nonwoven web. Next, they post-synthesized a secondary seeded growth of ZIF-8 on the prepared SiO$_2$/ZIF-8/PVP support [220]. The produced nonwoven composite webs and the secondary-synthesized membrane are shown in Figure 2.4 and Figure 2.5, respectively.

![Figure 2.4: SEM images of the ZIF-8/PVP composite fibers electrospun from methanol solutions of 12 wt% PVP and different seed concentrations: (a) 6 wt%, (b) 8 wt%, (c) 10 wt% and (d) 12 wt%. Reprinted from [220] with permission from Royal Society of Chemistry](image-url)
In-situ growth of ZIF-8 materials on flexible nylon membranes was also done using contra-diffusion method in the work of Yao et al. (2011). The two synthesis solutions were separated by a porous nylon membrane. The growth and crystallization occurred and developed on both sides due to favorable interactions between organic ligands of MOFs and polymers [221]. Figure 2.6 shows the schematic of contra-diffusion method and SEM image of the produced film.

In another study, Kuesgens et al. (2009) synthesized HKUST-1 in the presence of two kinds of pulp fibers, Kraft-processed and ChemoThermoMechanical pulp fibers (CTMP). The main difference between these two kinds of pulp fibers is the residual content of lignin after their production processing, with CTMP being less delignified. To synthesize, they solved trimesic acid in ethanol (EtOH)/DMF and then mixed it with an aqueous solution of Cu(NO₃)₂·2.5
H₂O. Afterward, 1 gram of pulp fibers was added to the solution and the solution was stirred for 15 min. The slurry was gradually heated to 85°C and kept at this temperature for 24 hours. By filtering and washing the product with EtOH/H₂O, the filtrate turned clear and blue fibers appeared. The fibers were briefly dried in air and activated at 160°C for 18 hours [218].

The direct growth and in-situ synthesis of HKUST-1 nanostructures on negatively charged silk fibers [203], unmodified and anionically-modified cellulose fibers [219], modified anionic woven cotton fabric [207, 219], and polyvinylamine (PVA)-modified woven polyester fabric [216] have also been reported in the literature. The possibility of synthesizing and direct growth of HKUST-1 on such pre-functionalized substrates is due to the presence of carboxyl groups on both the substrates and the synthesis solution [203, 207, 216, 218].

Direct growth of MOFs on ceramic [64], polyetherimide [222], porous alumina [223] hollow fibers, and etched stainless steel fibers [224, 225] is also reported. More interesting is the in-situ direct growth of MOFs in the presence of microporous AC [226], carbon nanofibers [227], single walled carbon nano tubes (SWCNT) [228, 229], carbon nanotube buckypapers (CNTBP) [230], and multi-walled carbon nanotubes (MWCNT) [231-233], with the main goal of improving hydrogen storage capacity.

The concept of (self) growth is also reported for carbon-based hybrid adsorbents, with no MOFs [234]. Szczypta et al (2009) improved the catalytic, separation, and storage properties ACF by self growth of CNT on them [235]. In another study, self-template growth of TiO₂ on carbon fibers was reported to increase the photocatalytic activity of the resulted hybrid carbon mat [236]. Zhou et al (2014) reported a higher electrical conductivity by Chemical Vapor Deposition (CVD) of CNT and carbon nano fibers on PAC [234].
2.3.5.2 - Characteristics and Considerations

Taking advantage of hydroxyl and carboxylic groups on cellulosic materials, they have been used as host media for embedding, immobilization and growth of different nanoparticles [207, 237-243]. Most of the literature that studied the in-situ growth of MOFs on textile substrates, specifically nonwoven media, is about synthesis of HKUST-1 on carboxyl-containing fibrous substrates [50]. The conversion of nitrile to carboxylic acid group is a necessity for the growth of MOFs on electrospun PAN nonwovens [107].

For instance, Kuesgens et al. (2009) found that the higher lignin content in CTMP pulp fibers results in higher degree of coverage by HKUST-1 based on the inherent affinity of lignin towards HKUST-1 crystals [218]. Pretreatment is not required if there is an inherent binding between the two components, like the binding between copper dimer and wool protein [216]. Hence, the presence of some kind of chemical pretreatment on the fibrous nonwoven substrate, or an inherent affinity between the components, is a necessity for attachment of MOFs to the substrate. Ensuring the proper chemical attachment of MOFs materials to fibers is confirmed by FTIR and/or XPS analyses [219].

The current focus of direct growth is on the fabrication of defect-free MOFs with controlled interface between the MOFs and interstitial gaps within the growing support [230]. Therefore, the controlled pore size within nonwoven structures is a vital matter of concern for processing of highly interconnected and freestanding MOFs hybrid structures [230, 244].

In general, such media are characterized by efficient adherence of MOFs to the substrate, regular distribution of functional particles on the substrate [216, 218], extended shelf life, and mechanical stability of the hybrid media [207, 216]. In-situ growth of MOFs on nonwoven media is advantageous since the porous structure of adsorbent is not shielded at all, corresponding to no loss of SSA. The total accessible surface area of individual fibers within the substrate determines the 3D uniformity of particles attachment [216] and the particle loading capacity. However, the crystallization and growth of MOFs follow an anisotropic fashion owing to the available space between the fibers and the 3D surface of each fiber.
Therefore, chemical compatibility and basic structural properties of the nonwoven web are important [50, 216].

Although the synthesis and incorporation of the adsorbent component take place at the same time, the main disadvantage of this method is its low throughput. Microwave irradiation [50] or ultrasound [203] synthesis techniques can enhance the production time; however, industrial-scale production of such media is not feasible.

2.3.6 - CoForming

2.3.6.1 - Implementation and Technology

Coform nonwoven webs are composite meltblown substrates that contain at least one additional-functional material, e.g., AC fibers/particles, pulp, super absorbent polymers (SAP). The technology was first introduced/patented by Kimberly-Clark Corporation where fiberized wood pulp was added to meltblown webs to increase the absorbency of the nonwoven [245].

Coforming is the introduction of functional component to meltblown stream(s) during the formation of meltblown web, e.g., blowing the particle/pulp into tacky meltblown filament stream [152, 246-249]. Coform nonwoven webs containing SAP have been widely used in diapers and wipes [248, 250, 251].

There are two general ways to create such structures: 1) providing a single stream of thermoplastic material to form the web and introducing the functional particles of interest to this stream; 2) providing two streams of meltblown filaments and introducing the adsorbent component at the convergence point of streams (impingement zone). Subsequently, the composite stream is deposited onto a perforated forming surface (drum or belt). Negative pressure is provided under the forming surface, and the solidified composite web is collected in the form of rolls [147, 251, 252].
Different devices are used to create, convey and introduce the stream of functional materials to filaments. These include picker roll and gas stream (common for AC particles) [252], carding system and airflow (common for ACF) [139], fluidized bed sprays [136, 152, 253], and particle shakers and compressed air [253].

Several configurations of coform process have been reported, most of which concern with the location and temperature at which adsorbent materials and meltblown stream(s) meet each other. Adsorbent particles are introduced from a feeding hopper to maintain a continuous incorporation [117]. In practice, particles are introduced to meltblown web stream at distances either far or close from the die nozzle [152, 251]. In addition, particles can have different temperatures adjusted according to the thermal properties of web material and particles’ thermal properties [117, 152, 247]. Based on the configuration, particles are mechanically entrapped within the meltblown web and/or thermally bonded to the filaments [251]. Coformed webs have minimal dusting. Laminating the hybrid web (2.3.8.4 -) with two or more spunbond nonwoven webs can further minimize dusting and enhance the mechanical properties [26, 136, 247, 251, 254-256].

Figure 2.7 demonstrates a configuration of a coform line where ACF is introduced to a single meltblown stream using a carding system coupled with airflow. ACF diameter was between 10 to 20 microns and their length was about one inch [139].
2.3.6.2 - Characteristics and Considerations

Coform technology can be viewed from two standpoints, web formation process and particle introduction/incorporation step. The processing parameters and techniques for the web formation are well described in the literature and are not the focus of this review [3, 68, 69, 257-265]. The following section focuses on the particle introduction/incorporation stage of coform process.

The most important parameter is the distance and location of the functional-component dispensing device relative to the meltblown die(s). This is important since not only can it change the velocity of particles at convergence point [139, 251], but also the filaments could be either tacky or non-tacky when particles hit them, depending on the polymer thermal properties [117].

Tackiness of filaments has profound effects on the mechanism by which particles are attached to filaments. Particles would thermally bond to tacky fibers and the resulted
meltblown web would mechanically entrap the particles, i.e. desired immobilization [248, 251, 252]. Otherwise, if fibers are completely solidified and non-tacky, the functional component is only mechanically entrapped within the web, at the contact points of microfibers [152, 246].

If particles are introduced to the web far from the die nozzle, three types of placements will be developed. A portion of the particles is in point contact with partially tacky fibers; some are mechanically entangled within the meltblown web interstices. The rest neither are in sufficient point contact nor mechanically entangled, resulting in fugitive particles (dusting) [117].

Particles can be introduced into the meltblown stream as the melt passes the die, when fibers are not fully consolidated [117, 247]. In this case, more binding and contact will be possible between the particles and fibers; however, the fiber stream and attenuation process are adversely affected by the particle insertion stream. Consequently, properties of the final meltblown structure and constituent fibers will diminish drastically.

Alternatively, in the case of heat-stable materials, the functional component is heated up to a temperature that approximates the temperature of fibers at die nozzle. (Heat-stable particles are any particles whose chemical, physical or other properties do not undergo substantial changes upon heating and the particle integrity/functionality would be maintained.) In this case, they are introduced into the fiber stream far from the nozzle where the web is partially formed and sufficiently stable. Partial penetration of the heated particles into the meltblown web renders a stable, non-dusting, composite web and leaves the non-penetrated surface of the particles available for adsorption [152, 247, 266, 267].

The velocities of meltblown filaments and particle streams and the difference between them are two other process parameters that should be controlled [248]. If the velocity of filament stream(s) at impingement zone is higher than that of the particles stream, the distribution of the adsorbent component is substantially homogenous within the nonwoven web. The higher speed of filaments stream(s), promotes enhanced turbulent mixing of adsorbent particles,
resulting in a consistent uniform particle distribution. However, higher speed of particle stream yields a gradient incorporation of particles within the nonwoven web [251, 252].

Huang et al. (2004) found three important processing parameters that could control the incorporation process and ACFs uniformity within the coform structure. (1) ACFs should have enough kinetic energy to be able to overcome the resistance of airflow and enter the fiber stream; (2) the kinetic energy of ACFs should be low enough so that the filament stream can arrest ACFs; and (3) the airflow must be adjusted to provide a uniform introduction of ACF to the meltblown web [139].

Convergence point is designed and located at the closest distance to the collecting surface to inhibit and minimize the dispersion of coform structure [248]. In addition, the relative angle of meltblown die(s) and dispenser influences the texture and extent of intermingling of the coform web [252].

Loading percentage of the functional component can be from 10% – 90% by weight of the composite coform. Loading percentage depends on the thermoplastic polymer properties and its crystallization rate, fiber diameter, and particle size [247, 248, 251-253].

One of the limitations of current filter media, as opposed to glass microfiber filters, is their large fiber diameter range. Large fiber diameter determines both the particle-loading capacity and the filtration performance. The average diameter of meltblown fibers is less than 10 microns [251], analogous to high available surface area for adsorbent component to adhere. The smaller the meltblown microfibers are, the more contact points between the functional particles and fibers [152, 246, 253]. Size of the particles can be 400 – 5 microns [247, 253]. Larger size of particles compared to microfibers enhances the mechanical entrapment of adsorbent component, measurable by shaking tests [253].

Since the strength of meltblown webs are relatively low, an optimum basis weight should be adopted to promote structural integrity [147]. Furthermore, the mechanical performance of meltblown core structure can be enhanced by sandwiching it between high surface area
lightweight spunbond layers that have higher strength. The composite web is calendared afterwards to fix the layers and particles [26, 90, 136].

In general, coform process is a high-throughput inexpensive method to produce composite webs. This is mainly due to the simultaneous production of the web and particle incorporation. In addition, attachment mechanism of particles to fibers can control the surface area loss.

2.3.7 - Electrospinning
2.3.7.1 - Implementation and Technology
There are three main techniques that lead to the formation of nanofibers, namely meltblowing, multicomponent spunbonding, and electrospinning [180, 268-270], with the latter yielding the finest fibers [81, 271-274]. Electrospinning technique, during its first years of development, was primarily concerned with production of polymeric nanofibers and complex nonwoven structures. During the last few years, electrospinning was investigated as a novel technique for production of nanoparticle-polymer composite nanofibers [275-281] and organic-inorganic molecular sieve nanofibers [282]. The process involves using an electric field to draw the fiber-forming polymer solution [272] to afford a nonwoven web structure composing of fibers with diameters down to few nanometers [79, 81, 271-273]. The resulted electrospun mats have shown great potentials for clean energy and water filtration applications [283, 284].

In a typical process, for instance, according to the target fiber diameter, the right amount of PAN is dissolved in N,N-dimethylformamide (DMF) [269, 285-290]; in hybrid structures the functional material of interest is added to the solution too [280, 285, 291-293]. Applying the optimal voltage to the solution [289], nanofibers are electrospun and collected on the target substrate [294]. In laboratory scale, the polymer solution is loaded into a syringe and drawn from its needle tip. In industrial scale, the polymer solution is drawn either from multiple pins [295] or from a roller-like electrode rotating in the solution bath [296].
To produce composite nanofibers, the polymer solution is mixed/loaded with the subject functional particles and then electrospun [269, 270, 290, 297, 298]. The resulting deposited nonwoven structure offers an excellent bed for immobilization of nanoparticles, used in filtration [270, 299]. This is in view of the following facts: (i) sufficient substrate flexibility; (ii) coexistence of high SSA nanoparticles and nanofibers; (iii) optimal distribution of nanoparticles in the electrospinning solution, thereby in the final composite structure [270]; and (iv) almost full accessibility to adsorbents' pores due to the very small fiber diameters relative to the adsorbent particle size [300].

Electrospinning solution precursors are from a vast variety of polymers, both synthetic and natural [281, 288]. However, polymers with high carbon yields, such as pitch [274, 301, 302] and PAN [286, 289, 303-305], are preferable for the formation of electrospun activated carbon nonwoven substrates.

In general, to produce a high-SSA activated carbon nonwoven substrate, the electrospun web undergoes a set of high-temperature transformational post-processes including stabilization, carbonization, and physical/chemical activation [274, 286, 288, 290, 303, 306-308]. Based on the precursor component materials, the collected web is stabilized (for 0.5 – 8 hours at 200°C – 350°C), carbonized (for 0.5 – 8 hours at 600°C – 1100°C), and subsequently activated (for 0.5 – 2 hours at 650°C – 2200°C) [288]. The activation process aims at the formation of pores. In physical activation, pores are formed due to the thermal degradation and removal of the activating agent at high temperatures [308-311]; whereas, in chemical activation, pyrolysis of the chemical agent and surface etching occur at lower temperatures [12, 36, 312]. The activation results in ultrafine porous AC nanofibers that are self-assembled into the shape of a nonwoven substrate for a variety of applications [285, 290, 302, 306, 313-317]. The high SSA and micropore volume of AC electrospun nanofibers enable applications in high capacitance electrical double-layer capacitors [290, 291, 293, 318-324], Li-ion battery separators [288, 291, 317, 325-327], storage of drugs [314] and hydrogen [307, 328-330], sensors [287, 302], catalysts [313], and adsorbents [316, 331-335].
Additionally, to further develop the surface area and functional sites on porous electrospun AC nanofibers, co-electrospinning has shown great potentials [288, 310, 311, 336]. Compared to the conventional electrospinning systems, the co-electrospinning solution is comprised of two immiscible polymers with miscible solvents. The mixed solution is electrospun using a coaxial spinneret into core-sheath or islands-in-the-sea composite nanofibers. Subsequently, the core component is dissolved or pyrolyzed to yield a high-SSA hollow porous-activated-electrospun carbon nanofiber [308, 310-312].

Although most of the studies regarding electrospun AC nonwovens deal with the fabrication of non-hybrid structures [288], there are cases where inorganic species [277, 288, 337], SWCNT [280, 338], MWCNT [302, 339-344], and AC particles and graphite [285, 303, 345] have been incorporated into electrospun AC substrates.

Hybrid MOF-nanofiber nonwovens, on the other hand, are produced via mixing the pre-synthesized MOF(s) particles in the electrospinning solution. In a typical process, MOFs crystals are synthesized separately and then dispersed uniformly in the electrospinning precursor solution [244, 300, 346]. The MOF-containing electrospun nanofiber is then electrospun and collected on the target substrate [294]. Some of these MOFs-containing hybrid structures have been used as the support for secondary direct growth (seed coating) of the mother MOF [244, 294, 347]. In the case of subsequent secondary seed growth, the hybrid substrate is placed in the mother-MOF synthesis reaction media (precursor solution in the autoclave vial) and undergone the hydrothermal/solvothermal synthesis steps [244, 294]. Alternatively, the base hybrid substrate can be impregnated and saturated by gradual addition (drop-by-drop) of the precursor solution, followed by solvent removal at high temperatures, to yield the seed-coated final substrate [347]. Hybrid MOF-nanofiber nonwovens have been investigated for different applications such as VOC and nitroaromatic sensors [244, 347, 348], separation and gas purification [244, 294, 300, 346], catalysis [294], and multicolor light-emitting devices [349].
The first attempt to use electrospinning solution as the polymer carrier for MOF materials was by Rose et al. (2011) [300]. They studied three polymer-solvent systems (polystyrene (PS)-tetrahydrofuran (THF), PVP-EtOH, and PAN-DMF) and two kinds of MOFs (MIL-100(Fe) and HKUST-1). Figure 2.8 shows the three different compositions of the MOF-polymer electrospun composite webs generated.

Figure 2.8: Images (A, C) and SEM micrographs (B, D, E, F) from electrospun MOF/fiber composites: (A) HKUST-1/PS fibers in relation to a human hair, (B) HKUST-1 crystal on a PS fiber analogue to a pearl necklace, (C) homogeneous MIL-100(Fe)/PVP layer on polypropylene non-woven, (D) MIL-100(Fe) particle in PVP fiber web, (E, F) HKUST-1 particles (BASF) in PAN fibers on a PAN non-woven (large substrate fibers in background). Reprinted from [300] with permission from John Wiley and Sons
MOFs can form nanosized assemblies in both single-phase (non-hybrid) and hybrid structures. Unlike organic polymers that can be processed into different desired shapes, e.g., fibers and sheets, MOFs are nonprocessable owing to the insolubility and often melting with degradation [350]. However, recently, one-dimensional formation of MOFs was reported [351-356]. The key is to, first, form amorphous coordination polymers [350], such as precursor solutions [357, 358] or gels [359-367]. Subsequently, the single-phase MOF nanofibers can be electrospun. Electrospinning is used to spin pure MOF nanofibers from water-/DMF-soluble Zn-based precursor solution [107]. Lu et al. (2001) reported that the MOF nanofiber size ranges from 60 nm to 4 microns, however the properties of nanofibers was not reported. The solubility of the complex, the key to the processability, depends on inclusion capability and hydrogen bonding interactions. This is generally achievable by introduction of BPE (4,4'-bis(pyridyl) ethylene) or BPY (4,4'-bipyridine) linear spacer ligands in the organic solvents [357, 358]. The production of MOFs nanofibers based on soluble precursors suffered from bad quality [368] and was not practically available in large-scale applications [350, 368]; therefore, electrospinning of gel-state MOFs complexes was considered [368]. Nickel-based MOF gel precursor was diluted by the addition of BPY and BPE to create a viscose solution that was electrospinnable in the absence of organic polymeric additives. The electrospun nanofibers were about 100 nm in diameter and showed promising properties for field emission applications [368].

Making hybrid adsorptive nonwoven webs is not limited to MOFs or AC nanofibers. A variety of adsorbent materials can be electrospun into hybrid nonwovens. These include zeolite nanofibers [282, 294, 369-384] and zirconia/PVP [219] composite electrospun nanofiber nonwovens.

It is worthy of attention that the similar hybridization concept have been applied to composite nanofibers made with the Forcespinning technology. Rotational movement of the spinneret applies centrifugal and hydrostatic forces to the mixed solution to initiate a liquid material jet. Jiang et al (2015) reported improved electrochemical properties in force-spun tin-containing carbon nanofibers [385].
2.3.7.2 - Characteristics and Considerations

In general, electrospinning is a simple efficient method to produce ultrafine high-surface-area fibers from a wide variety of polymers. The nanofibers can be easily functionalized and their compositional and morphological properties can be controlled by the choice of material(s) and process parameters [220, 270, 278, 279, 282, 325]. However, the process is low throughput, expensive, and the emission of hazardous solvents and fiber non-uniformity are some of the challenges [268, 288, 386, 387].

The right choice of precursor-solvent system and the optimal process parameters (such as applied voltage [288-290], TCD (tip to collector distance), solution flow rate [288, 290], and spinneret diameter [288]) are critical factors. Physical and chemical nature of the precursor-solvent system determines the boiling point of solvent [288, 350], the electrical conductivity of solution [287, 288, 314], and solution concentration [220, 270, 278, 279, 282, 288, 290, 325]. The latter, is influenced by the viscosity and surface tension of precursor-solvent and influences the morphology and diameter of electrospun nanofibers [269, 288, 290, 350]. Lower diameter of nanofibers can contribute to stabilization time, number of cross-junction points, substrate flexibility, SSA, pore volume, and pore accessibility. Higher SSA, pore volume, and pore accessibility are the keys to higher capacitance, catalytic performance, adsorption, and selective ion adsorption [287, 288, 292, 293, 319, 324, 332-334].

With regard to electrospun AC nanofibers, there are three pore development mechanisms, namely breaking, exfoliation, and expansion; the latter yields the desired fibrous porous structure [290]. Furthermore, pore size and uniformity of AC nanofibers are significantly affected by the size and dispersion of activating agent [288, 309, 342, 345].

In the case of hybrid AC nanofibers, the ultimate objective of hybridization is enhancing the pore formation and improving the conductivity of final structure [291, 293, 318, 322, 323, 342]. Pore formation takes place during the activation process based on different shrinkage-expansion coefficients of the nanofiber components [280, 285, 302, 338-345]. Moreover, the superior performance of electrospun AC nanofibers over its non-fibrous counterparts, i.e.
PAC and GAC, is attributed to their high SSA, porous, and fibrous morphology [292, 307, 333, 347].

AC nanofibers are inherently porous and high-surface-area; so the added component in hybrid AC nanofibers is not deemed to function as the adsorption sites. The functionality of the added component is to enhance the pore formation process. Therefore, "high" loading percentages of the functional component is not the sought-after processing parameter. Loading percentage of the functional component ranges between 0 – 4 wt.% [338] to 10 wt.% of the composite substrate [340]. Ju et al. (2008) found optimal loading percentage at 3 wt.% to reach uniform distribution, without agglomeration [342]. Haji et al. (2013) reported that the surface of hybrid SWCNT-AC nanofibers turned rough by adding more than 5 wt.% SWCNT [280].

Mechanical-physical properties of electrospun nonwoven web structure, such as flexibility and strength, depend on the nature of the precursor materials and processing conditions. Electrospun carbon fibers are too brittle and do not have sufficient flexibility which is required for a textile substrate, used per se in filtration application [301, 304, 388]. CNTs have high available interaction surface area and they have been reported to reduce the brittleness of AC nanofibers [288, 312, 332, 333, 342].

Loading percentage and loss of surface area for MOF-nanofiber hybrid nonwovens is based on different objectives. In this case, high-SSA MOFs are the prime adsorptive sites; hence, higher loadings and minimal loss of the SSA are sought-after. Hybrid MOF-nanofiber structures can be electrospun with initial loadings of 3 wt.% [347] to 5 wt.% [244]; subsequently, secondary seed coating can be done to increase the loading percentage.

Rose et al. (2011) found that the maximal loading of HKUST-1 in PS/THF was 40%. Two possible reasons were: i) the significant difference in polarity between the non-polar PS and polar HKUST-1, and ii) the small difference between particle size and fiber diameter. They could increase the MOFs loading up to 80% by using PVP as the carrier polymer. This web suffered from two important setbacks: (a) very low mechanical stability and (b) immediate
dissolution of the web upon contacting small amounts of water. The solubility of the web cannot be reduced by chemical cross-linking since MOFs offer low chemical stability. Hence, they chose a PAN/DMF solution and kept the loading at to 80%; this web did not suffer from water solubility. In this case, since the loading was 80% and the accessible MOF fraction was 78%, they concluded that no pore blockage happens [300]. Furthermore, Ostermann et al. (2011) reported that in the 56 wt.%-loaded ZIF-8@PVP electrospun nanofibers, the accessible ZIF fraction was 55.1 wt.%. This corresponded to almost full accessibility and zero pore blockage [346].

In conclusion, beside the advantages of electrospinning [347], the low throughput, low fiber diameter uniformity, and the environmental hazards inhibit the industrial application of electrospinning [268, 288, 386, 387].

2.3.8 - Other
2.3.8.1 - MOF Paper Sheets
Tailoring and engineering the structure of cellulosic paper sheets offer a suitable pliable structure. Their structure can adopt different geometries based on the desired production design. In addition, by choosing different pulp qualities or use of additives one can render the structure thick, permeable, hydrophilic, and/or rigid. These highly flexible design parameters afford paper-like bed structures for MOFs. MOF particles can be introduced into the paper sheet by adding fillers and/or pigments in paper forming technology [16]. For example, HKUST-1 powder was added to pulp slurry and introduced into paper sheets by the “Rapid Köthen” sheet mold process. Figure 2.9 shows an SEM image of the MOF-containing paper sheets.
It was observed that the slurry mixing approach yields reasonably-entrapped MOF composites. However, HKUST-1 crystals were inhomogeneously distributed on the MOF-containing paper sheets. The average content of MOF particles ranged between 6.5 to 14.6 wt. %, which is fairly broad. Thereby, particle distribution homogeneity needs improvement to make better MOF-containing paper sheets [16, 218].

2.3.8.2 - Mixed-Matrix Membranes Containing MOFs

The term Mixed-Matrix Membranes (MMMs) refers to membranes manufactured from two or more matrices. None of the matrices serves as the reinforcement component; however, each matrix material contributes specific properties to final composite structure [389, 390]. Perez et al. (2008) investigated Matrimid® [391] as the base scaffold for synthesis and growth of MOF-5 [392]. Matrimid® 5218 (polyimide of 3, 3', 4, 4'-benzophenonetetraacarboxylic dianhydride and diaminophenylindane) was chosen because of its attractive properties in gas selectivity, gas adsorption, high air permeability, excellent mechanical properties, high glass transition temperature, and high thermal stability [393].
To prepare MMMs and MOF-5, Perez et al. (2008) prepared the precursor solutions of both Matrimid matrix and MOF-5 and mixed them together with different weight ratios. After bath sonication and stirring the mixed matrix, they cast it onto a Mylar® A92 film and annealed it in a vacuum oven at 240°C for 24 hours. The thickness of the final MMMs was 35 microns and the SEM images of the prepared MMMs are shown in Figure 2.10.

![SEM images of the surface (a, d, and g), cross-section at low magnification (b, e, and h), and cross-section at high magnification (c, f, and i) of 10, 20, and 30% MOF-5/Matrimid® MMMs, respectively. Reprinted from [392] with permission from Elsevier](image)

Air permeability of the membranes increased with higher loading of MOF-5 and there was a great affinity between the Matrimid matrix and MOF-5 crystals [392]. Pressure drop, flexibility, and mechanical properties of the prepared membrane were not reported.
Additionally, successful spinning of PI–HKUST-1 blend is reported in the work of Hu et al. (2010) where they spun the PI–HKUST-1 composite into MMM hollow fiber by the dry/wet-spinning method [394].

2.3.8.3 - Charged Media

One way to incorporate adsorbent materials into nonwoven fibrous structure is by electrostatic charging. Either of the components, i.e. nonwoven substrate or functional materials, can be charged and then brought together. The "coated" substrate can then pass a thermal bonding process, such as calendaring, to fix the particles on the loaded web [2, 395].

In the case of charged powder particles, the target nonwoven substrate is ground and the charged powder is sprayed onto the web based on electrostatic attraction. The process involves the following steps: fluidization of the powder particles, charging the powder, and spraying the powder. The electrostatic properties of the target particles are of prime consideration [152, 396].

Important process parameters include: 1) charge distribution uniformity, 2) structural integrity of fluidized particles and nonwoven web, 3) electrostatic charging voltage, 4) control over particle loss during spraying, and 5) spraying distance, location, pressure, etc. [152, 396].

Fibroline™ is a commercially available process that utilizes the electrostatic charging concept to incorporate powders into fibrous substrates. The system is composed of two face-to-face electrodes that are connected to an alternative high-tension generator. The strong alternative electric field affords a homogeneous powder distribution inside the support. After scattering the powder onto the fibrous support, the layer is placed between two dielectrics and transported from one side to the other. Passed the alternative electric field, particles are accommodated within the web. It is claimed that the process does not cause any temperature build up in the substrate and no static electricity remains inside the material at the end of the
treatment. Dielectric properties of the particles play the most important role in this process (see Figure 2.11).

Figure 2.11: Schematic process of Fibroline™. Reproduced from [397]

The electrostatic/dielectric particle insertion process is ecologically advantageous in the sense that no chemical/binder agent is involved. This also promotes uncovered accessible surface/pore on the adsorbent [152, 396].

2.3.8.4 - Lamination
Lamination, sandwiching and bonding multiple layers of material for enhanced functionality, is the most common practice to make composite nonwoven filter media [1, 11, 398-401]. Fibrous layers can be chosen from a variety of processes, e.g., meltblown, spunbond, wetlaid, airlaid, carded. Depending on the nonwoven formation technique-configuration, layers can be laminated in-line with the production or in a post process. Likewise, the adsorbent component can either be applied in-line with the production or be formed separately beforehand and added later [116, 193]. A variety of bonding techniques can be applied, including: heat bonding or using hot melt adhesives, needle punching, hydroentangling, and ultrasonic bonding [3, 26, 402-404].
The functionality and properties of filter media can be improved by laminating composite layers within a single hybrid structure. However, the following processing parameters and issues should be taken into consideration: covered surface area of the absorbent component, structural damage and delamination, increased pressure differential through the filter depth, adhesion interference of particles in highly-loaded webs, stiffness, stability, and integrity of the hybrid medium [3, 26, 405, 406].

2.4 - GENERAL LIMITATIONS OF HYBRIDIZATION

2.4.1 - Surface Area Loss

The largest portion (> 95% [7, 12, 16]) of the surface area and pore volume in adsorbent materials is from the micropores, i.e. pores smaller than 2 nm. Based on the pore structure, e.g., slit-shaped, V-shaped, ink-bottle or neck-shaped, a large portion of surface area is accessible through transitional macropores, i.e. pores larger than 50 nm [7]. Therefore, it is conceivable that blocking just a few numbers of either of these pores would be at the expense of losing a considerable amount of SSA and pore volume [92, 407].

Choosing the suitable technique, one should deem that the accessibility of the surface area and porous structure is more important than the SSA itself. In general, the techniques in which the polymeric fiber and/or a binding agent fuse into the adsorbent are vulnerable of masking a portion of the pores. On the other hand, the media within which functional particles are only mechanically entrapped are vulnerable to dusting.

2.4.2 - Process Control

Due to the high surface free energy of the adsorbent materials [87], they need to be uniformly distributed and dispersed in the course of hybridization to avoid any agglomeration [92, 214, 216, 227, 342, 349, 408]. Thus, the functional component should be uniformly dispersed by some means, such as sonication [227, 342, 345, 349, 408] or magnetic stirring [207, 219,
Another process control parameter that is in mutual relation with agglomeration is the loading percentage. It is reported that the agglomeration is more likely to occur at higher loading percentages [342]. Furthermore, higher loading percentages can adversely influence the mechanical properties of the nonwoven, stability of the adsorbent materials on the polymeric substrate, breathability, and stiffness of the substrate [92, 214, 230, 288, 289].

Beside the uniform dispersion and loading percentage of functional particles, the amount of waste and environmental threat associated with each technique should be considered. In some processes, such as coforming, there should be an effective control over the dispensing of the functional materials. The most expensive component of a hybrid adsorptive filter is the adsorbent material and waste of these particles should be minimized. However, this is not the only reason that tight control on the particle loss is important. For instance, in case of conductive ACs and abrasive zirconia, the uncontrolled waste could potentially cause damages to the machinery. In addition, emission of solvent vapors in processes such as electrospinning should be controlled to reduce environmental hazard [269, 387].

### 2.4.3 - Extra Processes and Cost-Associated Issues

Some of the mentioned techniques require pre-/post-processes that add up to final unit cost. For instance, to directly grow the MOFs crystals on the substrate, some pretreatments are required that lengthen the production time and add up to the final cost. In some cases, to provide the hybrid nonwoven with optimal abrasion resistance and mechanical strength, the web would undergo the lamination process [2, 247, 254, 255, 299]. Therefore, the extra processes and their associated cost(s) should be considered carefully before choosing a method.
2.5 - CONCLUSIONS

We have reviewed the techniques to incorporate adsorbents (activated carbons and metal-organic frameworks) in nonwoven gas filtration media. Electrospinning and direct growth offer the highest adsorbent loading ranges and the least surface area coverage; however, they have a very low throughput. Wetlay process is not compatible with all adsorbents and compounded nonwovens cannot contain high loadings of adsorbents. Coating, thermal bonding, lamination, and coform are high-throughput hybridization processes. The major limitation of these techniques is the potential coverage of adsorbent surface area. The amount of the binding agent and the agent-particle surface interactions determine the coverage of adsorbents' surface area. The amount of molten polymer that fuses into the particles pores determines the surface coverage in thermal bonding and lamination processes. This amount depends on the polymer thermal properties, adsorbent loading%, temperature, and duration of thermal processes. Coform process offers an effective particle incorporation since the adsorbents are mechanically entrapped and partially bonded to the fibers.
CHAPTER 3: Improvement Opportunities for State-of-the-Art Adsorptive Filters
3.1 - STATE-OF-THE-ART ADSORPTIVE FILTERS, APPLICATIONS, AND LIMITATIONS

3.1.1 - Gas Phase

One of the most critical applications of gas adsorption is in respiratory systems. Half masks, full-face masks, and escape respirators use cartridges packed with GAC. The functional pressure drop in these "not-powered" air purifiers is the main challenge. Because of the limited available volume, high loadings of ACs (> 60% of mass of whole package) are packed into these canisters. This results in high differential pressure that may lead to channeling effects in the toxic effluent. Another problem is unsatisfactory adsorptive performance of ACs towards some reactive gases [409-411]. On the other hand, impregnated specialty ACs for adsorbing such reactive gases are very sensitive to humidity. This is because of the competitive adsorption of water molecules on these surface chemical groups [412-416].

Another popular application of adsorptive filters is in cabin air and HVAC filters; these are predominantly hybrid adsorptive nonwovens. The popular techniques to make these structures are wetlay (or airlay in case of ACF), coating, and laminating; the latter may be done for coated or carded webs. Many of them are not efficient incorporation techniques as they may compromise the adsorptive performance of the ACs. Coating and lamination (usually involves heat) can cover/mask the surface area and pore structure of ACs. Wetlay can adversely influence, or even exhaust, the chemisorption sites. Like most filter media, the balance between adsorbent loading and pressure drop is critical. Loading percentage is more vital for cabin air filters due to the confined and limited volume that is available for them in a vehicle. Last but not least, is the durability of filter in humid conditions [405, 417-421].

3.1.2 - Liquid Phase

Since liquid phase adsorption is not the focus of this study, only one common example is presented here, house drinking water filtration systems. Most of these filters are packed beds
of GAC or PAC and some wetlaid hybrid adsorptive nonwovens are available. The most important problem is inability of ACs to remove metal ions (fluoride, chloride, magnesium, etc.); AC cannot adsorb many metal ion to any significant degree. The other problem is fouling of the adsorbate molecules on AC surface that would diminish the filter practicality and create habitat for potential growth of microorganisms and bacteria. PAC leach out is another issue when pressure differential passes the standard limit [32, 33, 422-425].

3.2 - PROBLEM STATEMENT AND MOTIVATION

*Limited understanding of guidelines for fabrication of high-capacity low-pressure-drop hybrid adsorptive nonwovens*

Adsorptive filter media can separate toxic/unwanted molecules from the bulk stream, in our case NH$_3$ gas molecules from air stream(s) (choice of ammonia as the model gas is explained in Section 3.4.1 -). Hybrid adsorptive nonwovens fall into one category of these media and they are composed of two main components: adsorbent material(s) and fibrous nonwoven support(s).

The ammonia adsorbent is required to have a certain level of hygrothermal-chemical-mechanical stability. Adsorbents with acceptable mechanochemical stability are available. However, irreversible chemisorption of H$_2$O molecules decreases the durability and/or adsorption capacity of NH$_3$ adsorbents in humid conditions (RH > 40 %). Low hygrothermal stability of NH$_3$ adsorbents acts as the bottleneck in the expansion of their applications. Many studies are trying to address this issue; but solutions to this low stability were beyond the focus of our study.
The nonwoven support has two key functionalities, alleviate the pressure drop and contain high loadings of adsorbent in a uniform/stable fashion. This study was based on the room for improvement in this area.

In general, important properties/requirements of hybrid adsorptive nonwovens include:

- Lower pressure drop than their packed bed counterparts;
- Sufficient amount of adsorbent for the filter lifetime (loading %);
- Stable incorporation (minimum shedding) of the adsorbent component(s);
- Accessible adsorbent surface area and pore structure (least surface area blockage);
- Uniform distribution of adsorbent component(s) within the nonwoven structure;
- Structural integrity of the hybrid media according to the operational condition(s);
- Assessed adsorptive performance/capacity of the hybrid adsorptive media (evaluation of adsorption capacity is critical for both adsorbent and hybrid media).

There are interactions between the above-mentioned properties/requirements. For instance, a less open medium can contain larger amounts of particles in a stable fashion but would create higher pressure drop. Binders can entrap the particles in a more open medium but they would cover the adsorbents' surface area and reduce accessible adsorption sites. Therefore, for improving any of these qualities one should consider not only each individual property, but also its interaction with other properties.

All of the mentioned qualities are desired for both gas and liquid adsorptive filters. However, methods to improve any of them and approaches to solve related issues are application-driven; so is the choice of adsorbent.

The focus of this study is on gas adsorptive filters and some of the issues that this study addressed are as follows:

- As discussed in Section 3.1 -, most of the studies (prior art) fail to address the relationship between the stability and accessibility of adsorbent component(s) within hybrid nonwoven media. Generally, actual bonding between adsorbent material(s) and
fibrous support increases the mechanical stability of the particles within the structure. These bonding points cover the surface area of adsorbent(s) and decrease the accessibility to the pores and adsorptive functionality. The motivation was to establish a relationship between particle stability and pore accessibility and a method to do so in gas adsorptive filters.

- The relationship/balance between pressure drop and filtration efficiency is a common argument in the filtration field. Structural parameters of air/liquid nonwoven filters play the most important role in enhancing pressure drop-filtration efficiency balance. In the case of adsorptive gas filters, adsorbents' parameters, i.e. loading %, size distribution, and uniform distribution, exercise significant influence on this balance. The motivation of this study was to establish a relationship between pressure drop, filtration efficiency and adsorbents' parameters.
- In addition, the relationship between the adsorptive performance of adsorbent(s) and comprised hybrid web was not well understood. Adsorption capacity of adsorbents is usually evaluated in controlled environments where actual hybridization conditions (high temperature, humidity, solvents, chemicals, etc.) are missing. In most cases, it is assumed that adsorbents would have the same adsorption capacity after incorporated in a nonwoven structure. The motivation was to confirm if these assumptions are reasonable; and if not, whether the loss of adsorptive functionality can be predicted/compensated.

Considering the issues above, the identified objectives (Section 3.2 -) and adopted approaches (Section 3.4 -) are discussed in details later in this chapter. The main motivation behind this project was to improve gas adsorptive nonwoven filters. The following examples, using ammonia gas filtration, provide a clearer picture of the mentioned possibility.

The first example refers to respiratory applications where hybrid adsorptive nonwovens seem to be promising media to substitute for packed bed canisters. In case of single-use escape masks, NIOSH requires stringent regulations/standards for ammonia filtration (see Table 3.1). Figure 3.1 demonstrates the comparison of standard operational ranges for NH₃ escape masks versus AVON-C50 canisters. The region connected by white lines offers potential
room for improvement, longer saturation times (> 30 min) and lower differential pressure (< 6 mm w.g.).

Figure 3.1: Ammonia escape mask operation: (green) NIOSH standard, (red) AVON-C50, (white) room for improvement

The second example is for cabin air filters (CAF), for which standards were presented in Table 3.1. Figure 3.2 shows the regions for CAF standard requirements and state-of-the-art Purafil-Puracarb ® AM filters. There is a considerable potential for improvement where longer service lifetimes (> 3.5 months) and lower pressure drops (< 7 mm w.g.) would be conceivable; this region is specified by white connected lines.
3.3 - OBJECTIVES

The main goal of this study was to establish the necessary requirements for hybrid nonwovens to contain adsorbents effectively. To accomplish so, the problem was divided into three major objectives, discussed in this section. Although some of the concepts/approaches might be translatable to liquid filtration applications, the focus is limited to gas filtration.

3.3.1 - Adsorbent Selection for Adsorption of Anhydrous Ammonia

There are many adsorbents for ammonia adsorption in the gaseous phase (see Section 3.4.1 -) and they have different physiochemical properties. These properties have huge impact on the process parameters used for their incorporation. Their chemical structure and their affinity toward ammonia determine their durable functionality and adsorption capacity, respectively. Therefore, our first objective was to select a suitable model adsorbent for ammonia to study.
the process parameters and adsorptive performance of the final hybrid structure. As mentioned earlier, the superior performance/durability of the adsorbent was not the focus for this objective.

3.3.2 - Incorporation Technique: Selection & Evaluation

The opportunities and challenges are different for available incorporation techniques (see Section 2.3 -). In addition, the compatibility of the technique with the selected adsorbent and the process parameters are of great importance. Ammonia adsorbents chemisorb NH₃ gas molecules. They also tend to chemisorb water molecules through the same adsorption sites. In most cases, this is an irreversible process; so, wetlay technique cannot be employed for NH₃ adsorbents. Coating, compounding, and thermal bonding techniques can potentially cover a large portion of the surface area and adversely influence the functionality. Direct growth and electrospinning are promising; however, they offer very low throughput values. Therefore, we hypothesized that coform process (see Section 2.3.6 -) would be a suitable technique for incorporating the model NH₃ adsorbent in nonwoven fabrics.

There are three components to study in a coform process, meltblowing process, particle (functional material) dispensing process, and interaction/combination of the two. Two meltblowing configurations, i.e. single-beam and dual-beam, were investigated. In addition, presence of any foreign element in the meltblowing system, such as a particle dispenser or pressurized air, might interfere with the web production process. Any potential perturbation could influence the physical/structural properties of the web. Therefore, particle dispensing process and its interaction with meltblowing web production is studied.

Three methods were considered to incorporate adsorbents in the coform process: gravity-fed lawn spreader, coform "control box", and particle shaking. Elements of interest included operational parameters of each process, influence of process on web quality, and particle parameters (such as size, density, charge, nominal loading percentage, etc.).
Physical-structural properties of hybrid webs determine the influence of particle dispensing system on web quality; they also enable us to establish process-structure-property relationships. They include two types of information, adsorbent-related (such as actual loading percentage, bonding stability/durability, etc.), and web-related (such as thickness, basis weight, air permeability, etc.). The objective was to study the effects of incorporation process parameters on hybrid nonwoven filtration properties.

Therefore, the second objective was to select and evaluate a proper particle dispensing system, its parameters, and its influence on the produced web. Feasibility of passive-fed supply systems was investigated for single-beam and dual-beam meltblowing configurations.

3.3.3 - Evaluation: Adsorptive Properties of Adsorbents and Hybrid Webs

In order to address the relationship between adsorbents’ stability and accessibility within the structure it was crucial to evaluate adsorptive properties of adsorbents and hybrid webs. There are two aspects to adsorptive performance of adsorbent(s) and hybrid webs, their adsorption capacity and their available surface area.

Evaluation/comparison of adsorption capacity/affinity of particles and hybrid webs provides an understanding about the effects of hybridization process and nonwoven structure on adsorbents. During the hybridization step, exposure of adsorbent to high temperatures and/or toxic environment could adversely influence the adsorption capacity.

Available surface area provides information on actual bonded areas between the particles and fibers. This is important for evaluating the hybridization step and its efficiency. Therefore, adsorptive performance of particles and hybrid webs provide valuable insight into the functionality of adsorbent(s) when incorporated in nonwoven structures. Therefore, the third objective was to evaluate the ammonia adsorption capacity and surface area analysis of the adsorbents and hybrid webs.
Example

For instance, translation of identified objectives into a final product is provided for respiratory applications. This involves converting a packed bed of activated carbon granules (Figure 3.3.a) to a multilayer hybrid adsorptive nonwoven (Figure 3.3.b). As an example, let us assume that the bed depth (2.5 cm) was filled with layers of hybrid nonwoven, total area of ~ 1.125 m². Assuming a 150-g/m² nonwoven that contains 50% (by weight) NH₃-adsorbent (adsorption capacity 160 mg g⁻¹), the cartridge would saturate after 66 minutes @ standard conditions. The counterpart cartridge would saturate before 30 minutes.

![Figure 3.3: (a) disassembled ammonia escape mask versus (b) AC-NW composite web](image)

3.4 - APPROACH

The research approach was to incorporate a model ammonia adsorbent in a model nonwoven web, study the particle dispensing methods in coform process, and evaluate the adsorptive/structural properties of the final hybrid web. The final hybrid web would have application(s) in NH₃ gas adsorptive filter media. It was hypothesized that the results would enable us to establish the necessary requirements for hybrid nonwovens to contain adsorbents effectively.
Results of this approach included both quantitative and qualitative elements. Each module/objective was accomplished individually; elements and variables are elucidated when necessary. The remainder of this chapter discusses the variables for each objective, the methods to collect and analyze the data, and the outcome.

### 3.4.1 - Model Pollutant Gas and Model Adsorbent

*Model Pollutant Gas*

There is a growing environmental awareness with regard to the removal (and/or recovery) of pollutant gases from bulk gas streams. Adsorptive gas filters should remove the target pollutants and to evaluate their performance it is necessary to choose a model pollutant. There are few criteria to consider for selecting such model gas; these include:

- The importance of its threat to the environment;
- The removal difficulty/issue with the current adsorbents;
- The commercial availability for techniques/methods to sense/detect such a molecule;
- The low safety and handling issues when dealing with such gas on a lab scale.

Like many other gases, ammonia represents a serious threat to air quality. The anthropogenic release of anhydrous ammonia from agricultural and manufacturing industries, sewage treatment plants, refrigeration facilities, and on-road vehicles adds up to the natural emission resources. Since this gas is a serious threat to human health (eye, skin, and respiratory system), EPA has recently set stringent regulations on NH$_3$ emission levels [20, 426-438].

Activated carbons, as the current commercial adsorbent for gas purification/filtration, have very limited removal efficiency for ammonia. Ammonia is a reactive gas that would only chemisorb on adsorbent materials. Chemisorption of NH$_3$ on ACs requires impregnated (chemically activated) ACs; uniform functionalization (impregnation) of ACs is large quantities is difficult to achieve. Aside from ACs, many non-conventional NH$_3$ adsorbents are emerging and they suffer from low stability and/or adsorption capacity [414].
Many NH₃ sensors and detectors are commercially available since constant emission monitoring is required by EPA’s Clean Air Act (CAA); these are electrochemical and/or PID (photoionization detector) sensors. In addition, analytical instruments such as gas chromatography units are available to study [NH₃] (ammonia concentration) accurately.

NIOSH (National Institute for Occupational Safety and Health) and NRC (National Research Council) have limited the exposure to ammonia to a time-weighted average concentration (TWA) of 25 ppm and short term limit concentration (STEL) of 35 ppm [431]; the immediately dangerous to life and health limit (IDLH) is 300 ppm. Adsorption capacity tests would be done in chemical hoods at concentrations as low as 50 ppm that is well below IDLH.

In conclusion, anhydrous ammonia was selected as the model pollutant gas; standard test methods and popular adsorbents for NH₃ are discussed in the next section.

Standards

To have an understanding about methods and parameters for evaluating hybrid adsorptive filter, two potential applications were considered, escape mask respirators and cabin air filters. Table 3.1 demonstrates the standard test methods for evaluation of NH₃ adsorptive performance of mentioned filters.

Table 3.1: Standard test methods to evaluate NH₃ adsorptive performance of escape masks (NIOSH 2014) [439] and cabin air filters (ISO 11155-2 and 1) [440]

<table>
<thead>
<tr>
<th>Test Parameters</th>
<th>Flow rate (Lpm)</th>
<th>[NH₃] (ppm)</th>
<th>Influent RH%</th>
<th>Influent temp. (°C)</th>
<th>Differential pressure (mm w.g)</th>
<th>Service life (minutes)</th>
<th>End of service life (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIOSH 2014</td>
<td>64</td>
<td>2500</td>
<td>25 ±5</td>
<td>25 ±2.5</td>
<td>&lt; 75</td>
<td>15, 30, 45, 60, 90</td>
<td>50</td>
</tr>
<tr>
<td>ISO 11155-2</td>
<td>5000</td>
<td>30</td>
<td>50 ± 2</td>
<td>23 ± 3</td>
<td>&lt; 102</td>
<td>Reported</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Important test conditions/parameters are flow rate, influent concentration, temperature, and humidity. Important performance criterion is saturation capacity (adsorption capacity) at the
specified test conditions. Of course, these are industrial levels for testing and evaluation and some parameters may be compromised when doing them on a lab scale.

*Adsorbents for anhydrous NH₃*

Commercially, the most predominant adsorbent for ammonia is activated carbons that are impregnated with phosphoric acid. They may be used with a combination of other adsorbents in a single product but they are the responsible component for adsorbing NH₃. As mentioned throughout this review/introduction, the major problem of these functionalized ACs is their reduced efficiency in presence of moisture [414].

On the lab/research scale, however, the variety of NH₃ adsorbents is too numerous to list. Therefore, some adsorbents that are studied the most are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacities (mg g⁻¹)</th>
<th>Limitation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST</td>
<td>113</td>
<td>Structural instability is moisture, irreversible adsorption</td>
<td>[20, 414]</td>
</tr>
<tr>
<td>IRMOF-3</td>
<td>105</td>
<td>&quot;</td>
<td>[20, 23]</td>
</tr>
<tr>
<td>MOF-74</td>
<td>122</td>
<td>&quot;</td>
<td>[20, 441]</td>
</tr>
<tr>
<td>COF-10</td>
<td>255</td>
<td>Low dynamic adsorption</td>
<td>[442]</td>
</tr>
<tr>
<td>Silica gel 40</td>
<td>134</td>
<td>&quot;</td>
<td>[442, 443]</td>
</tr>
<tr>
<td>13X Zeolite</td>
<td>153</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>187</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

*Adsorbent Selection*

The choice of adsorbent(s) is application-driven. For instance, high-capacity adsorbents that are hygrothermally unstable are suitable for single-use applications (such as respirators). However, more stable adsorbents are promising for filters with longer lifetimes. The field of application, in our case gas, is another determining factor.

In this project, we studied two types of adsorbents to select the model ammonia adsorbent, one non-conventional adsorbent (such as MOFs and/or zirconia) and one commercially
available activated carbon. Adsorption capacity, application in gas field, hygrothermal stability, and commercial availability were parameters of interest. Adsorption capacity was confirmed by adsorption tests (chapter 5:) and application/stability was confirmed by market/literature research. The result was a model adsorbent for ammonia that would be used for the next objectives.

### 3.4.2 - Evaluation of Gas Adsorption Filters

Adsorption performance of the adsorbents/hybrid webs was the final target of this study. This would be studied from two aspects, surface area analysis and NH$_3$ adsorption capacity.

Surface area analysis was done with ASiQ instrument from Quantachrome. Parameters of interest are BET specific surface area, mean pore diameter, total pore volume, pore size distribution, and degree of microporosity. These tests would be done on the model adsorbent (of different sizes) and the hybrid webs. Quantitative results would provide information about the effects of adsorbent size and hybridization on adsorbents' microporosity.

NH$_3$ adsorption capacity tests were done with a lab-built dynamic adsorption test rack (features are explained in detail in chapter 5:). These tests were done on a group of adsorbents to choose the model adsorbent. Control nonwovens and hybrid webs would be tested as well. The outcome of these tests would be values for NH$_3$ adsorption capacity at the set testing conditions. Quantitative results would provide information about the effects of testing protocols and hybridization process on materials' adsorption capacities.

### 3.4.3 - Hybridization Techniques through Coform Process

The coform process (meltblowing system + particle dispensing system) was chosen because it was compatible with our adsorbent particles and because meltblown webs offer unique air filtration properties. Noteworthily, the application of the proposed coform system has not
been investigated in prior art. The approaches to investigate the components of this technique are as follows.

3.4.3.1 - Melting Process
Meltblowing involves many complex process parameters that are not the focus of our study. Two meltblowing configurations, i.e. single-beam and dual-beam, were used for adopted coform technique. Some related parameters involve number of blown filament rows, collector drum's vacuum pressure, die to collector distance (DCD), and relative angles/converging point in case of using two beams. These parameters were investigated as they have significant effects on the produced web. The result would be the optimal meltblowing configuration and parameters.

3.4.3.2 - Particle Dispensing: Process and Parameters
Particle dispensing methods should be compatible with the adsorbent. For high-quality hybrid web, the method should provide continuous uniform flow of particles. Lawn spreader, coform "control box", and particle shaking were compatible with our particles.

Continuity and uniformity of particle discharge would determine the proper concept/method. This is investigated quantitatively by measuring the weight of discharge with respect to time.

Process parameters of the above-selected method should be studied to find optimal dispensing conditions. These parameters include particle size and density, discharge location/angle relative to polymer stream(s), particle flow rate, and dispensing air pressure in case of pressurized chute. The result would be a uniform particle dispensing method and its optimal conditions.
3.4.4 - Analytical Techniques and Results

To investigate the effect(s) of foreign element(s) in the meltblowing system, such as a particle dispenser or pressurized air, physical-structural properties of the hybrid web were studied. These include basic web properties (such as thickness, basis weight, etc.), fiber size distribution, SEM micrographs, adsorbent loading percentage, and filtration properties (air permeability and pressure drop). These are some preliminary-proposed types of tests and the final tests may vary depending on the hybrid web quality. Qualitative and quantitative results would help understand the hybridization parameters and efficiency.
CHAPTER 4: Model Adsorptive Medium and Application Feasibility of HKUST Metal Organic Framework (MOF)
4.1 - INTRODUCTION

Adsorbents are exposed to a variety of harsh conditions and/or stresses in industrial applications, such as mechanical, chemical, and hygrothermal. Criteria for a model adsorbent in this study were application in gas filtration, hygrothermal stability, and high NH$_3$ adsorption capacity (> 20 mg g$^{-1}$ for reliable detection when measured by the adsorption test apparatus described in chapter 5). To select a model adsorbent for adsorption of gaseous ammonia, two potential materials were studied; specialty activated carbon from Calgon Carbon (Ammonasorb) and PAC-HKUST composite MOF. Ammonasorb (AM) was studied for its application in the coform process and HKUST was studied because of its potential application for in-situ synthesis.

Activated carbons are the most popular conventional adsorbents with proven functionality in gas adsorption filtration [12]. Physically activated carbons have high adsorption capacity (> 33% of their weight) for most nonreactive gases; this occurs through non-specific physisorption. In case of reactive gases, such as NH$_3$, specific chemical activation is required to chemisorb the target molecule [411].

There are numerous examples of "non-conventional" adsorbents for ammonia (see Section 1.3.3 -). Almost all of these novel structures have very limited industrial applications in the presence of moisture [20, 414]. Most of adsorbents have lower NH$_3$ adsorption capacity in humid conditions. However, adsorption capacity of some adsorbents is higher in humid environments; this is due to dissolution of NH$_3$ molecules in the thin layer of adsorbed water in the micropores [414]. In general, structural collapse in humid environments (RH > 40 %) is the predominant reason that hinders the industrial application of non-conventional adsorbents [196-199, 201, 444].

HKUST MOF is widely studied in the literature for its high ammonia adsorption capacity. Like many other adsorbents from MOFs' family, HKUST has structural instability in the presence of moisture. It is worth mentioning that NH$_3$ adsorption capacity of HKUST has been reported to be 90 – 170 mg of ammonia per gram of adsorbent (mg g$^{-1}$) [414].
Addition of activated carbon powder (PAC) to MOFs synthesis solution has been shown to create some synergic effects. Microporous activated carbons can potentially adsorb water molecules and decelerate structural transformation in HKUST. Not-functionalized activated carbons have almost no adsorption capacity toward ammonia.

To investigate the synergic effect between PAC and HKUST, mother HKUST and composite PAC-HKUST were synthesized. Surface area analysis (microporosity) and color change were correlated to the synergic effect between PAC and HKUST. Microporosity of samples would provide information about any potential structural transformation. Color change in HKUST would provide insight into the coordinative state of its copper sites, i.e. saturated versus unsaturated sites. Irreversible chemisorption of H\textsubscript{2}O molecules in HKUST usually accompanies by color change from dark blue to light blue; this is due to the change in the vibration of copper-copper bond [414].

### 4.2 - MATERIALS AND METHODS

Some of the incorporation experiments/trials were done just as proof of concept; so, different model particles were used for these trials. Model particles include PAC, microsphere hollow glass beads (MSGB - from Potters Industries LLC, Malvern, PA), and coconut granular activated carbon (CGAC); latter is the feedstock for AM. Table 4.1 shows the properties of PAC, AM, MSGB and CGAC.

Table 4.1: Physical properties of PAC, AM, MSGB and CGAC

<table>
<thead>
<tr>
<th>Material</th>
<th>Size range, mean</th>
<th>Apparent density (g cc(^{-1}))</th>
<th>Relative density (g cc(^{-1}))</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>&lt; 150, 37 (\mu)m</td>
<td>0.32 – 0.37</td>
<td>0.31 – 0.52</td>
<td>pH: 6 – 8</td>
</tr>
<tr>
<td>AM</td>
<td>2.3 × 4.7 mm</td>
<td>0.5</td>
<td>0.4 – 0.7</td>
<td>&lt; 20% H\textsubscript{3}PO\textsubscript{4}</td>
</tr>
<tr>
<td>MSGB</td>
<td>&lt; 81, 46 (\mu)m</td>
<td>0.14</td>
<td>0.23 – 0.27</td>
<td>pH: ~ 5.6</td>
</tr>
<tr>
<td>CGAC</td>
<td>2.3 × 4.7 mm</td>
<td>0.45</td>
<td>0.4 – 0.7</td>
<td>–</td>
</tr>
</tbody>
</table>
Ammonasorb Activated Carbon

Ammonasorb is a coconut granular activated carbon (CGAC) from Calgon (see Figure 4.1) that is chemically impregnated/activated with phosphoric acid to chemisorb ammonia [445-448]. AM is commercially available and many commercial gas filters in North Americas and Europe use it for NH\textsubscript{3} chemisorption. Commercial availability was a plus for AM as a model adsorbent.

Figure 4.1: SEM micrographs of AM and its feedstock (CGAC)
**PAC-HKUST composite MOF**

Synthesis of HKUST was done according to the work of Yaghi [23, 39]. Mixture of (1.75 g) copper nitrate and (37.5 ml) de-ionized water (stirred @ 200 rpm for one hour) was added to a mixture of (1.05 g) trimesic acid and (37.5 ml) ethanol (stirred @ 200 rpm for one hour). The solution was stirred vigorously @ 500 rpm for 2 hours and then filled in a Teflon-lined autoclave. The autoclave was heated up to 100°C in an environmental chamber and held in there for 24 hours. The blue product was filtered out for the next step, three washing cycles. To wash out any unreacted solvent(s), the precipitate was stirred vigorously in a 1:1 water/ethanol washing bath (two hours @ 500rpm). The product was filtered and dried at room temperature for 20 hours. The dried HKUST powder was then activated in a vacuum oven @ 200°C for three hours.

Synthesis of PAC-HKUST composite was similar to HKUST synthesis, with the difference of adding 70 mg of PAC (3.5 % by weight) to the synthesis solution. The autoclave was heated in a rotary IR heat beaker machine to promote uniform dispersion of PAC during the synthesis. The PAC was commercial food-grade powdered AC from Multavita, Castle Valley, MT (see Table 4.1 for properties) with no additional functionalization.

SEM micrographs, surface area/microporosity analysis, and color change were used to investigate the synergic effect between PAC and HKUST. Microporosity analysis data included BET specific surface area (SSA$_{BET}$), total pore volume (V$_t$), volume of mesopores (V$_{meso}$), volume of micropores (V$_{mic}$), and micropore contribution (V$_{mic}$/V$_t$). These parameters were studied for as-prepared samples and for "aged" samples. Aging refers to keeping the samples in closed-cap vials in room conditions (25±5°C and 55±10 RH %) for 40 days.
4.3 - RESULTS
Figure 4.2 shows the SEM micrographs and actual samples and Table 4.2 shows the microporosity analysis for as-prepared and aged mother HKUST and composite PAC-HKUST, measured by our ASiQ BET instrument (from Quantachrome, Boynton Beach, FL).
Figure 4.2: SEM micrographs (scale bar = 50 µm) and actual materials: a) PAC, b) as-prepared HKUST, c) aged HKUST, d) as-prepared PAC-HKUST, e) aged PAC-HKUST
Table 4.2: Microporosity parameters of as-prepared and aged HKUST and PAC-HKUST

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA\textsubscript{BET} (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>$V_\text{t}$ (cc g\textsuperscript{-1})</th>
<th>$V_{\text{meso}}$ (cc g\textsuperscript{-1})</th>
<th>$V_{\text{mic}}$ (cc g\textsuperscript{-1})</th>
<th>$V_{\text{mic}}/V_\text{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>1610</td>
<td>0.877</td>
<td>0.232</td>
<td>0.645</td>
<td>73%</td>
</tr>
<tr>
<td>as-prepared HKUST</td>
<td>865</td>
<td>0.458</td>
<td>0.061</td>
<td>0.397</td>
<td>87%</td>
</tr>
<tr>
<td>aged HKUST</td>
<td>362</td>
<td>0.162</td>
<td>0.076</td>
<td>0.086</td>
<td>53%</td>
</tr>
<tr>
<td>as-prepared PAC-HKUST</td>
<td>907</td>
<td>0.492</td>
<td>0.078</td>
<td>0.414</td>
<td>84%</td>
</tr>
<tr>
<td>aged PAC-HKUST</td>
<td>394</td>
<td>0.199</td>
<td>0.088</td>
<td>0.111</td>
<td>56%</td>
</tr>
</tbody>
</table>

Microporosity ($V_{\text{mic}}/V_\text{t}$) of aged HKUST and aged PAC-HKUST decreased by almost the same amount compared to as-prepared materials. These structural disintegrations were also obvious in SEM micrographs. In addition, the color change from dark blue in as-prepared to lighter blue in aged samples was obvious. It was concluded that addition of PAC without any special functionalization did not decelerate the structural collapse in HKUST.

**4.4 - MODEL ADSORBENT SELECTION & MODIFICATION**

Water molecules competitively chemisorb to the same adsorption sites that are available to bind NH\textsubscript{3} molecules. Such behavior is a prominent problem for ammonia adsorbents in the presence of moisture. This is an inevitable fact for almost all NH\textsubscript{3} adsorbents and it was not a criterion for our model adsorbent.

Although the number of NH\textsubscript{3} adsorption sites may decrease due to bound water molecules, the structural integrity of the adsorbent is also important. HKUST undergoes structural disintegration if exposed long enough (~ two weeks) to such conditions [444]. Structural stability of the materials was important for our model NH\textsubscript{3} adsorbent. Therefore, HKUST or composite structures made from HKUST were not chosen for our study. However, semi-crystalline structure of ACs remains intact when exposed to moisture [411]; this structural stability was an important criterion for the model adsorbent.
Ammonasorb was chosen as the model ammonia adsorbent in this study. This is based on its application in gas filtration, commercial availability, high NH$_3$ adsorption capacity, and structural stability in the presence of moisture.

AM was used for two different modules of this research, (I) establishing the effect of test conditions and calibration of the dynamic adsorption test apparatus (chapter 5), and (II) studying the feasibility of particle incorporation in the coform process, developed at NWI. The as-received AM required some grinding before its application for the above modules; this was because of its large original (2.3 × 4.7 mm).

Hammer mill was used to grind AM granules; this was done in Pulp and Paper Eng. Dept. at College of Natural Resources at NC State University. This was followed by particle size distribution via gradual sieve shaker at the same facility. The granules were ground for 3 minutes and mechanically sieved for 10 minutes. The hammer mill sieve size was 2 mm and there were six mesh sizes available for particle size distribution, US#20: 850 µm, US#25: 710 µm, US#40: 425 µm, US#80: 180 µm, US#100: 150 µm, and US#200: 75 µm. To ensure the process consistency, this was done 2 times (runs). Figure 4.3 shows the size distribution and cumulative size distribution of the ground AM particles.

![Figure 4.3: Ground AM particles: (a) size distribution and (b) cumulative size distribution](image)
It was concluded that the grinding process had a yield of > 90% and more than 70% of the ground particles were larger than 425 µm; the stability of the process was confirmed by doing two runs. All coform experiments with ground AM were done with AM batches received after March 30, 2015.
CHAPTER 5: Dynamic Adsorption of Ammonia: Apparatus, Testing Conditions, and Adsorption Capacities

This chapter is a manuscript entitled “Dynamic Adsorption of Ammonia: Apparatus, Testing Conditions, and Adsorption Capacities”, by Hooman Amid, Benoît Mazé, Michael C. Flickinger, and Behnam Pourdeyhimi, and will be submitted to the Journal of Hazardous Materials.
5.1 - INTRODUCTION
Continuous release of toxic gas molecules and ever-growing environmental concern for clean air highlight the importance of gas filtration [432, 434, 436-438]. Removal of these molecules requires high surface area adsorbent materials such as activated carbons (AC) [7, 11, 35, 449]. Application of adsorbents depends on their adsorption capacity for the target molecule(s) under the operational conditions. Therefore, evaluation of adsorption capacity of different adsorbents and filter media is highly dependent on the testing conditions and methods [10].

Standard test methods for adsorption filtration include ISO 11155.2, ASHRAE 145.2, and NIOSH 42 CFR 84. Compliance with these standards is expensive because they require expensive gas-specific sensors, and large amounts of material for research on newer adsorbents such as MOFs (metal organic frameworks) [53] and COFs (covalent organic frameworks) [450]. Hence, more than 95 % of evaluation of prototype adsorbents is conducted on small-scale test apparatus to minimize adsorbent and gas-sensor costs [20].

However, large discrepancies between published capacity results and lack of test reproducibility, as determined by statistical analysis resulting from different testing methods, hinder comparisons. In the case of ammonia adsorption by HKUST MOF, reported capacities range from 90 to 170 mg of NH$_3$ per gram of HKUST. These values are based on one-specimen tests and are not statistically sound [20, 23, 451]. The chemistry, characterization, and adsorption process of HKUST- NH$_3$ is well-studied [414], however, little is known about why such discrepancies exist.

In addition, most studies have only focused on two testing conditions, temperature and humidity. The influence of other operational conditions such as inlet ammonia concentration ([NH$_3$]), residence time (RT), adsorbent size, samples initial state (preparation), and sample aging [414, 443, 452-456] is missing.

This study utilizes an inexpensive adsorption test apparatus and carefully calibrated hand-held gas sensors to identify the sources of overestimated adsorption capacities and
discrepancies; model gas was NH$_3$ and model AC adsorbent was Ammonasorb™. Careful calibration of the test apparatus using calibration gas standards and triplicate measurements for each test ensured accuracy and precision. This small-scale adsorbent testing apparatus is translatable to other gas-adsorbent testing systems as hand-held sensors can be fabricated for multiple gases.

5.2 - MODEL POLLUTANT AND MODEL ADSORBENT

One example of toxic gas molecules is ammonia (NH$_3$) that is released to our environment from agriculture-manufacturing industries and sewage treatment plants. Ammonia is a reactive gas and the number of studies concerning its threat is growing in both academic and industrial worlds. Therefore, ammonia was the model toxic gas for this study [430, 431, 433, 435, 457].

Activated carbons (AC) and silica are examples of conventional adsorbents; Ammonasorb is a commercially available granular AC for NH$_3$ adsorption. MOFs and COFs are examples of newer-class adsorbents; HKUST is the most popular MOF that is studied for NH$_3$ adsorption. Ammonasorb™ (AM) from Calgon Carbon Corporation Pittsburgh, PA was the only model adsorbent in this study. AM is a phosphoric acid-impregnated AC (6×12 US Mesh). The vendor claims that, based on the operational conditions, the adsorption capacity of AM is between 70 mg g$^{-1}$ to 160 mg g$^{-1}$. Table 5.1 shows the pore characteristics of AM measured by our ASiQ BET instrument (from Quantachrome, Boynton Beach, FL).

<table>
<thead>
<tr>
<th>BET specific surface area (m$^2$ g$^{-1}$)</th>
<th>Total pore vol. (cc g$^{-1}$)</th>
<th>Mesopore vol. (cc g$^{-1}$)</th>
<th>Micropore vol. (cc g$^{-1}$)</th>
<th>Micropore content</th>
</tr>
</thead>
<tbody>
<tr>
<td>659</td>
<td>0.272</td>
<td>0.047</td>
<td>0.225</td>
<td>83 %</td>
</tr>
</tbody>
</table>
5.3 - PROPOSED ADSORPTION TEST APPARATUS

The industrial analytical tool, used for adsorption capacity tests, is gas chromatography (GC). GC can accurately monitor the inlet and/or outlet gas concentrations in both in-line and off-line modes. Using two in-line units to measure the inlet and outlet gas concentrations provides analytical precision; however, this equipment can be expensive [458]. Therefore, it was worthwhile looking at inexpensive alternatives, e.g., hand-held gas detectors, while taking into consideration their limitations.

The main components of the proposed dynamic adsorption test set up were inlet NH$_3$ detector, digital flow indicator, and outlet NH$_3$ detector (see Figure 5.1). The inlet detector was in-line, before the adsorbent bed. It monitored and recorded NH$_3$ concentration in 2-second increments during the tests. The digital flow indicator measured and recorded the volumetric flow of the inlet right before the adsorbent bed. The gas detectors (GasBadge Pro from Industrial Scientific) used electrochemical sensors, with reading resolution of 1 ppm between 0 to 500 ppm. In addition, the adsorbent bed was a 6.35 mm inner-diameter stainless steel tube.

![Figure 5.1: Schematic of the adsorption test apparatus](image-url)
Figure 5.2 demonstrates a typical test result from the proposed test equipment. The blue curve shows the inlet [NH₃] and the red curve is for the outlet [NH₃]. To measure the amount of adsorbed ammonia, the area above the red curve was subtracted from the area below the blue curve; this is the area between the two curves, $A_{bc}$.

![Figure 5.2: Typical test result from the adsorption test apparatus](image)

Equation 1 was used to calculate the adsorption capacity [414, 455].

$$A_{t+dt} = A_t + dt \times (C_0 - \frac{C_t + C_t + dt}{2}) \times \frac{Q_{air}}{m_{ads}} \times \frac{M_{gas} \times 273}{10^6 \times 22.4 \times (273 + T)}$$

Equation 1

$$A_s = \sum_{t=0}^{t_s} A_t$$

- $A_t$ = adsorption capacity at $t$ (mg per g of adsorbent)
- $A_s$ = saturation capacity (mg per g of adsorbent)
- $t$ = time (min)
- $t_s$ = saturation time (min)
- $dt$ = time interval between two points of the adsorption curve (min)
- $C_0$ = inlet concentration of ammonia on Detector # 1 (ppm)
- $C_t$ = outlet concentration of ammonia at $t$ on Detector # 2 (ppm)
- $m_{ads}$ = weight of adsorbent's bed (g)
- $Q_{air} = \text{total flow rate (ml min}^{-1}\text{)}$
- $M_{gas} = \text{gas molecular weight (g mol}^{-1}\text{)}$
- $T = \text{temperature (°C)}$

The most important observation was the lag time for the inlet detector measurements. This lag time can cause fundamental errors (overestimation) in the results that are obtained from electrochemical single-detector adsorption test units. The potential overestimation could be up to 60 %, the orange area in Figure 5.3.

Most of the prior literature would adjust their target inlet concentration using the apparatus flow meters. It was assumed that the adjusted flow meter setting would provide similar inlet concentration for each test. Our results showed that this was not necessarily true. Even five percent change in the temperature/humidity of the lab results in inconsistent flow meter reading. In single-detector systems, this would result in false assumptions about the inlet $[NH_3]$ that translates to even higher overestimations.

![Figure 5.3: Potential overestimation in single-detector test units](image)
5.4 - CALIBRATION AND TEST SETTINGS EFFECTS

5.4.1 - Calibration

To calibrate the testing apparatus and to evaluate its accuracy, 25 "empty-bed" experiments were conducted in 5 days, to check the impact of changes in house air temperature and humidity. Average ammonia concentration of 50 ppm was chosen to comply with ASHRAE 145.2 and ISO 11155.2 standards. Table 5.2 shows the conditions for each day.

Table 5.2: Test conditions for the calibration stage

<table>
<thead>
<tr>
<th>Day</th>
<th>Temp. (°C)</th>
<th>RH%</th>
<th>Inlet [NH₃]</th>
<th>Flow rate (lpm)</th>
<th>Run time (min)</th>
<th>Avg. readings diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19±0.5</td>
<td>19±1</td>
<td>49±3 ppm</td>
<td>0.25±0.01</td>
<td>20</td>
<td>±6.5 ppm</td>
</tr>
<tr>
<td>2</td>
<td>20±1</td>
<td>24±0.8</td>
<td>50±2.5 ppm</td>
<td>0.24±0.01</td>
<td>20</td>
<td>±4.8 ppm</td>
</tr>
<tr>
<td>3</td>
<td>23±0.5</td>
<td>22±2</td>
<td>49.5±3 ppm</td>
<td>0.25±0.01</td>
<td>20</td>
<td>±4.9 ppm</td>
</tr>
<tr>
<td>4</td>
<td>23±0.5</td>
<td>21±1.5</td>
<td>52±3 ppm</td>
<td>0.25±0.02</td>
<td>20</td>
<td>±4.5 ppm</td>
</tr>
<tr>
<td>5</td>
<td>20±1.5</td>
<td>23±1</td>
<td>51±1.5 ppm</td>
<td>0.25±0.01</td>
<td>20</td>
<td>±6.9 ppm</td>
</tr>
</tbody>
</table>

Detectors readings were monitored and the difference between them was plotted over time (Figure 5.4). The average of readings difference did not show any specific correlation to the above condition ranges.

![Image of Figure 5.4: Difference between the detectors' readings](image)

The difference between detectors' readings averaged at ±5.5 ppm. Based on the average inlet [NH₃], 50 ppm, the accuracy of the results was defined at ±11%. Establishing this measurement error was critical to correct interpretation of results (full details in Appendix A).
5.4.2 - Testing Conditions and Effects

Testing conditions and settings are critical to the adsorption capacity of materials. The adsorption test apparatus, shown in Figure 5.1, allowed for setting the following parameters. Their effects on NH$_3$ adsorption capacity of baked Ammonasorb (b.AM) were tested and are presented (b.AM: Ammonasorb baked at 110°C for 3 hours and cooled to room temperature in a desiccator prior to test). Note: while studying any setting or parameter of interest, all other test conditions were constant (Table 5.3). Each test was done for three specimens and results represent the average value.

Table 5.3: Basic test conditions

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RH%</th>
<th>dew point</th>
<th>volumetric flow</th>
<th>Residence time</th>
<th>inlet [NH$_3$]</th>
<th>adsorbent mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>21±3°C</td>
<td>22±3</td>
<td>0±4°C</td>
<td>0.25±0.02 lpm</td>
<td>36 ms</td>
<td>50±5 ppm</td>
<td>32±2 mg</td>
</tr>
</tbody>
</table>

➢  **Humidity – ranging from 10 to 75 %**

Two different settings were applied to investigate the impact of dry conditions (RH % of 10 – 15 %, T = 21±1.5°C, and DP = 0±3°C) and humid conditions (RH % of 65 – 75 %, T = 21±1.5°C, and DP = 18±3°C).

Adsorption capacities of Ammonasorb (AM) at humid and dry conditions are shown in Table 5.4. Adsorption capacity of Ammonasorb decreased by 73 % in the humid challenging stream. This was attributed to the higher affinity of water molecules, as opposed to NH$_3$, to the adsorption sites. Presence of water molecules has a complex impact on adsorption that depends on the adsorber-adsorbate system. For instance, Petit et al (2012) reported an increased capacity at humid conditions (RH 70 %) for HKUST MOF. Formation of thin water film on HKUST pore surface enhanced the adsorption of NH$_3$ through dissolution of NH$_3$ molecules in water. However, competition (adsorption energy) between H$_2$O and NH$_3$ molecules in humid challenging gas may result in decreased adsorption capacity. Therefore, behavior of adsorbent-adsorbate system in humid conditions determines the effect of humidity on adsorption capacity.
Table 5.4: Influence of humidity on adsorption capacity of Ammonasorb

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>CV%</th>
<th># of runs</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.AM</td>
<td>65.3</td>
<td>8.26</td>
<td>3</td>
<td>Dry</td>
</tr>
<tr>
<td>b.AM</td>
<td>17.9</td>
<td>7.66</td>
<td>3</td>
<td>Humid</td>
</tr>
</tbody>
</table>

- **Inlet \([\text{NH}_3]\) – ranging from 0 to 400**

Two different settings were applied to investigate the impact of low inlet concentration ([\(\text{NH}_3\)] = 50 ppm) and high inlet concentration ([\(\text{NH}_3\)] = 400). Upper limit for measurements was chosen at 400 ppm since the detection limit of the sensor was 500 ppm.

Table 5.5 demonstrates the adsorption capacity of AM at high (400 ppm) and low (50 ppm) inlet \([\text{NH}_3]\). The capacity was higher at the higher inlet concentration that is in agreement with the literature [459]. This phenomenon was explained by Henry's law, i.e. higher possibility of adsorption at higher differential pressure (concentration).

Table 5.5: Adsorption capacity vs. inlet \(\text{NH}_3\) concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>CV%</th>
<th># of runs</th>
<th>Inlet ([\text{NH}_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.AM</td>
<td>121.6</td>
<td>6.47</td>
<td>3</td>
<td>400</td>
</tr>
<tr>
<td>b.AM</td>
<td>65.3</td>
<td>8.26</td>
<td>3</td>
<td>50</td>
</tr>
</tbody>
</table>

- **Residence time – ranging from 5 to 50 ms**

Four different settings (flow rates) were applied to investigate the impact of Residence time (RT) (9, 18, 27, and 36 ms). RT was calculated according to Equation 2.

\[
RT = \frac{D \cdot A}{Q} \quad \text{Equation 2}
\]

Where "\(D\)" is the adsorption bed depth (cm), "\(A\)" is the bed cross-section area (cm²), and "\(Q\)" is the flow rate (cm³ ms⁻¹).

Adsorption capacity was directly correlated to the RT (see Figure 5.5). This correlation agreed with the prior literature and the adsorption mechanism explains the reason [460].
Adsorption of ammonia on impregnated AC is a chemical reaction and is done through chemical adsorption, i.e. chemisorption. The reaction time depends on the molecule-surface interactions and many other factors. The longer exposure time to the adsorber's surface results in more adsorbed species. However, depending on the adsorber-adsorbent system, this relationship plateaus at some point [7, 8, 12]. The information about adsorption kinetics is critical to the design and engineering of actual filter media.

![NH₃ adsorption capacity vs. residence time](image)

Figure 5.5: Influence of residence time on adsorption capacity

### 5.5 - REPRESENTATIVE ADSORPTION TESTS

After establishing the impact of test settings on adsorption capacities, the influence of the following factors was examined: sample preparation, aging, and sample granule size.

To evaluate the effect of **sample preparation**, AM was baked at three temperatures for 3 hours. Generally, sample baking helps remove water molecules and other contaminants from adsorption sites. Based on the reported baking temperatures in the literature [24, 441, 443, 452, 455, 461, 462], 90°C, 100°C, and 110°C were chosen. For each test, a fresh sample, right out of the sample jar, was baked. The baked sample was transferred to a desiccator immediately to cool down to room temperature without re-adsorbing moisture.
Aging studies were conducted for two sample conditions, fresh AM (f.AM: right out of jar with no baking) and aged AM (a.AM). Aging of AM was done by exposing the fresh sample to controlled lab conditions for 24 hours, i.e. 22±1°C and RH % of 40±5.

One of the common applications of adsorbents is in composite adsorptive filters. Depending on how adsorbents are incorporated in these media, they should have particular size ranges [27]. Effect of granule size on the adsorption capacity was investigated by grinding the carbon. Four size ranges included the original AM (3360 – 1680 µm) and the ground AMs, 500 – 425 µm, 180 – 150 µm, and < 75 µm.

5.6 - RESULTS AND DISCUSSIONS

Influence of sample preparation and aging

Table 5.6 shows NH₃ adsorption capacities for fresh, aged and baked samples. Adsorption capacities did not show meaningful difference between the fresh sample and samples baked at 90°C and 100°C. Baking AM at 110°C for 3 hours resulted in highest adsorption capacity. This was explained by removal of water molecules and other organic contaminants from the adsorption sites and leaving vacant sites for NH₃ molecules. Hence, the same preparation protocol was used for all other experiments.

In addition, a.AM showed 51 % decreased capacity that was explained by exhaustion of adsorption sites by water molecules and other organic compounds. The aging data is important for estimating the durability of adsorptive filters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>CV%</th>
<th># of runs</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>f.AM</td>
<td>49.1</td>
<td>2.75</td>
<td>3</td>
<td>Not-baked</td>
</tr>
<tr>
<td>AM</td>
<td>47.8</td>
<td>5.53</td>
<td>3</td>
<td>90°C for 3 hr</td>
</tr>
<tr>
<td>AM</td>
<td>53.7</td>
<td>4.10</td>
<td>3</td>
<td>100°C for 3 hr</td>
</tr>
<tr>
<td>b.AM</td>
<td>65.3</td>
<td>8.26</td>
<td>3</td>
<td>110°C for 3 hr</td>
</tr>
<tr>
<td>a.AM</td>
<td>31.8</td>
<td>0.04</td>
<td>3</td>
<td>No</td>
</tr>
</tbody>
</table>
Influence of sample granule size

Grinding and breaking the AC granules would create new surfaces that were not exposed to impregnation during the chemical activation process. Figure 5.6 demonstrates this phenomenon for Ammonasorb AC. Grinding did not cause a considerable drop in adsorption capacity of particles larger than 150 µm. However, the adsorption capacity of the powdered AM (< 75 µm) decreased significantly (around 32 %). This was explained by the creation of surfaces that did not contact the phosphoric acid during the impregnation step. Hence, before incorporating ground particles into filter media, potential drop in adsorption capacity should be investigated.

![NH₃ adsorption capacity vs. particle size](image)

Figure 5.6: Influence of residence time on adsorption capacity

5.7 - CONCLUSIONS

This study highlights why there are discrepancies and overestimation in the prior NH₃ adsorption capacity literature. Results show that the gas-sensor's lag time could lead to overestimated adsorption capacities (60 %) in single electrochemical gas-detector units. In addition, these results suggest that the measurement tolerance of gas detectors could cause ±11 percent error. Overestimations were eliminated by using two calibrated hand-held NH₃ detectors, one for inlet and one for outlet. Results show that baking the adsorbent (AM: Ammonasorb™) prior to testing has a significant influence on adsorption capacity. There
was a direct relationship between residence time and amount of chemisorbed NH$_3$. Adsorption capacity was higher at higher inlet [NH$_3$], and humidity (70 % RH) reduced (73 %) the capacity of AM. Ground AM (> 150 µm) did not lose its adsorption capacity; but AM powder (< 75 µm) lost 32 % of its capacity. This method can provide guidelines for accurate measurements of adsorption capacity and comparison of different types of adsorbents using hand-held gas-specific sensors. The calibration protocol that was developed for this small-scale adsorption apparatus identified the measurement tolerance and resulted in confident conclusions. The proposed testing procedure and calibration protocol are translatable to other gas-adsorbent systems as hand-held sensors are available for a variety of gases. Future studies include testing the capacity of adsorbents embedded within filter media using this apparatus.
CHAPTER 6: Formation Feasibility of Particle-Meltblown Nonwovens:
Passive Particle Supply to Single Meltblowing Beam
6.1 - INTRODUCTION

Coform method is a high-throughput one-step technology to produce hybrid nonwovens, i.e. functional material(s) incorporated in meltblown fabrics while they are forming. DuPont was the first company to patent the concept of coform process in the early 60s [463] that was further improved by 3M and Kimberly-Clark in the 70s [246, 464]. Two major coform configurations include the active introduction of functional component(s) to a) one thermoplastic filament stream (single-beam, see Figure 6.1.a), or b) in between two thermoplastic filament streams (dual-beam, see Figure 6.1.b). Active dispensing methods utilize compressed air supply to deliver the functional components (particles and/or fibers) to the thermoplastic filament stream(s) [27, 136, 139, 152, 253].

![Figure 6.1: Schematic of coform process, a) single-beam [245, 247] and b) dual-beam [252]](image)

Meltblowing and particle delivery processes are well established in prior studies [463-477]; however, the influence of active feeding systems (compressed air) on web formation and properties are not discussed. Compressed air jet and polymer stream(s) converge at a point where filaments are not fully solidified; therefore, web formation is susceptible to disturbance. In addition, less than 20% of the single-beam coform processes have studied the
incorporation of particles, and these particles have a mean diameter larger than 200 µm. Rest of the coform studies are about incorporating staple fibers, mainly wood pulp fiber. In either of the cases, the amount of particle or fiber loss during the process is not reported [463-477].

It was hypothesized that active particle feeding can disturb the web formation and properties. Therefore, this chapter focuses on the feasibility of formation of single-beam coform structures via passive particle feed, i.e. gravity fed. Criteria for a successful single-beam passive-fed coform process were minimal particle loss and negligible change in web basic properties (CV% of basis weight). Model particles were gravity-fed on a commercial meltblowing line to examine particle loss. Due to excessive particle loss, a controlled incorporation volume was suggested and its application was evaluated based on its influence on web properties.

6.2 - MATERIALS AND METHODS
6.2.1 - Polymer and Model Particles
Polypropylene (melt flow index 30) was used for all experiments. To provide and examine the proof of concept, two model particles were microsphere glass beads (MSGB) and powdered activated carbon (PAC) (see Table 4.1 for details).

6.2.2 - Meltblowing Facilities and Configurations
Biax meltblowing spinnerets were used for all of the single-beam (sb) experiments (see Figure 6.2). The gravity-fed experiments were done at Biax Fiber-Film Corporation in Appleton WI (BFC-sb). The controlled-volume experiments were done at The Nonwovens Institute (NWI-sb).
Conventional meltblowing systems attenuate the molten polymer stream(s) through two knives (or jets) of hot air (see Figure 6.3) [478]. However, in Biax spinnerets, each polymer nozzle/capillary/orifice is encompassed by its own air nozzle (see Figure 6.4). Individual filaments are shielded by their own hot air jet that delays the interaction between the ambient air and hot attenuating air. According to the manufacturer, this results in more uniform and stronger fine fibers [479].
As mentioned earlier and in Section 3.2, the objective of this study was to investigate the feasibility of single-beam passive-fed coform process. Therefore, only relevant meltblowing process parameters were studied; these included die-to-collector distance (DCD), vacuum pressure, die pressure, and converging angles. Figure 6.5 shows the applied configurations for the BFC-sb trials.
6.2.3 - Passive Particle Dispensing

For the gravity-fed experiments on BFC-sb, a lawn spreader was used to introduce a free-fall curtain of model particles (PAC). The discharge rate was regulated based on the number of revolutions per minute (rpm) of the spreader's motorized brush.

For the NWI-sb controlled-environment experiments, it was proposed to create a controlled volume in front of the die and to investigate the ability to control the incorporation process and waste powder. Using a coform "control" box was proposed to achieve the mentioned goal that has not been reported in the prior art. The idea was to place a control box between the die and collector to create an enclosed controlled environment where particles can be fed from a slit in the top of the box. The high velocity of air/filament streams inside the box would create suction (negative pressure) on the top slots. This would provide the opportunity to introduce particles to polymer stream without using an external and additional airflow.

Different volume geometries were investigated to find the optimal conditions; Figure 6.6 shows these geometries. Optimal conditions refer to volume geometries that would not disturb the fiber/web formation process.
To find the proper geometries, multiple filament strings were attached to the die and tracked during "cold runs" (meltblowing with no polymer or heat). The geometry that showed the least perturbation or disturbance on the filament strings was chosen for the trials. To study the influence of control box on meltblown webs, two sample webs were produced, one with the control box (BW) and one without (CW). MB process conditions for both webs were identical, DCD: 30 cm, air pressure: 8 psi, and vacuum pressure: 50%.

Basis weight and mean flow pore diameter were studied to compare the physical-structural properties of CW and BW. Basis weigh measurement is one of the most widely used techniques to study the uniformity along and across nonwoven webs [480]. Basis weight was measured in 12 equally distributed locations across the width of the sample, "A" being the far left and "L" being the far right side of the web. Along the samples, 30 measurements were done for each location (see Figure 6.7).
6.3 - RESULTS AND DISCUSSIONS

Passive (gravity) feed of powdered activated carbon (PAC) on BFC-sb was not possible since the polymer-attenuating air-jet blew the powder away. This happened in all meltblowing process conditions (Figure 6.5) and all particle discharge locations. It was concluded that PAC (mean particle size of 37 µm and largest particle size of 150 µm) could not be gravity-fed in the BFC-sb coform configuration.

Among 12 configurations of the coform control box, BI-TI+ geometry (truncated pyramid-diverging profile towards the collector) showed no filaments drag towards the top and bottom sides of the box. Drag towards the left and right sides was not observable; Figure 6.8 shows this geometry during the web formation time.

Another parameter that influenced the disturbance inside the box was the amount of open area at the box inlet near the die (green area in Figure 6.8). The negative pressure inside the
box would drag air from around the die, protecting the filament streams from sticking to the box sides. Regardless of the box geometry, filaments would be dragged and stick to the box sides if there was no open area at the inlet.

Figure 6.8: Truncated pyramid profile (BI-TI+) and open area of the coform control box

Figure 6.9 demonstrates the distribution of average basis weight along the length and across the width of the CW and BW samples.

Figure 6.9: Basis weight distribution, (a) along, and (b) across the CW (control) and BW (with box) samples
Figure 6.10 shows the coefficient of variation (CV%) of basis weight along and across the CW and BW webs.

![Figure 6.10: CV% of the basis weight, (a) along, and (b) across the CW (control) and BW (with box) webs](image)

Table 6.1 demonstrates the influence of using the control box in NWI-sb meltblowing process.

**Table 6.1: Influence of using coform control box in web basis weight uniformity (control web: CW, and web with box: BW)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Basis weight (g m⁻²)</th>
<th>CV% of basis weight along the length (%)</th>
<th>CV% of basis weight across the width (%)</th>
<th>Web width (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>CW</td>
<td>BW</td>
<td>CW</td>
<td>BW</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>29</td>
<td>4.84</td>
<td>13.50</td>
</tr>
<tr>
<td>Difference</td>
<td>-18%</td>
<td>+177%</td>
<td>+242%</td>
<td>+39%</td>
</tr>
</tbody>
</table>

Application of the coform control box showed a significant effect on the nonwoven basis web uniformity. The dragging action of vertical sides of coform box resulted in considerable increase in web width. Although filaments did not stick to the box, the huge increase in basis weight CV% suggested substantial perturbation of fiber-web formation process. Careful studies of the turbulent flow inside the box might help improve-optimize the process; however, this was not the focus of our study.
Mean flow diameter of the nonwovens were tested using a Capillary Flow Porometry equipment, and GalWick as the fluid (surface tension = 15.9 dyne cm⁻¹). Only one specimen was tested from each web. The mean flow pore diameter was 41.5 µm for CW and 46.6 µm for BW. Although these values were not statistically sound, they were in agreement with the stretched structure of the BW sample.

As discussed in the Introduction, studying the influence of the particle feeding system on web formation properties is critical, and this was missing in the prior literature. Results stress the importance of studying and verifying that the particle incorporation means are not influencing the web properties adversely. This was a significant finding for our future trials. It also provides guideline for other researchers in this field.

6.4 - CONCLUSIONS
This chapter focused on the feasibility of producing single-beam coform webs via passive-feed particle incorporation. It was concluded that small gravity-fed PAC particles (< 150 µm) did not entrain the polymer stream, and were blown away from the filaments. This was due to the unfavorable interaction between small powder particles and attenuating air jet. It was hypothesized that a control coform box could create a controlled incorporation volume and allow for filament-particle intermixing. Using the coform control box disrupted the web formation process, changed the web basis weight, and increased the basis weight non-uniformity. It was concluded that the influence of particle incorporation means, such as the control box and/or air-jet fluidized particles, on web properties must be investigated for viable and stable hybridization process.
CHAPTER 7: Formation of Activated Carbon-Meltblown Nonwovens:
Passive Particle Supply in Dual-Beam Coform Process
7.1 - INTRODUCTION
Formation of hybrid functional nonwovens via a dual-beam coform process is very popular. Since hybrid nonwoven media have critical applications in consumer goods and sorptive filtration markets, practical knowledge about them is important. Based on the materials and process parameters, these coform webs form stable structures that are engineered to deliver target product specifications (e.g., pressure drop, sorption capacity, and filtration efficiency). Figure 7.1 shows several configurations of the dual-beam coform process. Chapter 2 reviews some of the important active-particle-fed coform process parameters and their influence on the structure; two of them are relative particle velocity and particle discharge location. Lower particle velocity relative to polymer streams forms structures with uniform particle distribution in the z-direction; higher particle relative velocity forms gradually-loaded structures (different particle loadings on each side of the web). With respect to particle discharge location, particles can converge with tacky filaments upon polymer exit from spinneret, or where solidified filaments are laying on the collecting surface. Particles adhere (heat-bonded) to tacky fibers and get mechanically entrapped between solidified filaments [27].
Coform process parameters for active particle feed are well established in the prior art. However, the influence of such active feeding systems on web properties and the feasibility of passive particle supply have not been reported. To the best of our knowledge, there is no public information about fabrication of coform webs via dual-beam Biax spinnerets. In addition, less than 30% of dual-beam coform processes have studied the incorporation of particles; the majority of them focus on wood pulp fiber. In either of the cases, the amount of particle or fiber loss during the process is not reported. Although particles are incorporated in a controlled manner, almost all of these structures require post-processing, such as lamination and heat press, to achieve higher particle stability [249, 251, 484-491].
It was hypothesized that active particle feeding can disturb the web formation and properties. In addition, it was hypothesized that two meltblowing streams would counteract each other’s turbulent airflows and allow for successful particle incorporation in their between (would not blow away the particles). Therefore, this chapter focuses on the feasibility and methods of formation of dual-beam coform structures via passive particle feed, i.e. gravity fed. In general, criteria for successful particle incorporation are as follows:

• Minimal or ideally no particle waste;
• Minimal or ideally no perturbation in the fiber/web forming process;
• Effective bonding between the MB layers (minimal or ideally no delamination);
• Effective comingling of particles with the webs (minimal or ideally no particle shedding from the final web).

To examine the feasibility of such process, model particles were gravity-fed on a commercial meltblowing line. Upon successful proof of concept, a uniform and contiguous particle discharge was achieved via a shaker-chute configuration. The influence of the incorporation means (shaker-chute) on web properties was investigated and verified through CFD (Computational Fluid Dynamics) simulations and experimental data. These web properties included web’s basis weight uniformity, fiber diameter (distribution), and filtration efficiency.

7.2 - MATERIALS AND METHODS
7.2.1 - Polymer and Model Particles
Polypropylene (melt flow index 30) was used for all experiments. To provide and examine the proof of concept, two model particles were microsphere glass beads (MSGB) (from Potters Industries LLC, Malvern, PA) and powdered activated carbon (PAC – from Multavita, Castle Valley, MT) (see Table 4.1 for details). Ground Ammonasorb AC (AM)
was used to verify uniform and continuous particle flow on the shaker-chute assembly, and to accomplish the main coform trials (see Table 7.1).

Table 7.1: Ground Ammonasorb size ranges

<table>
<thead>
<tr>
<th>Sample Size range (µm)</th>
<th>AM–75</th>
<th>AM–300</th>
<th>AM–425</th>
<th>AM–710</th>
<th>AM–850</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>&lt; 75</td>
<td>300 – 425</td>
<td>425 – 710</td>
<td>710 – 850</td>
<td>850 – 2000</td>
</tr>
</tbody>
</table>

7.2.2 - Meltblowing Facilities and Configurations

As mentioned earlier and in Section 3.2 -, the objective of this chapter was to investigate the feasibility of dual-beam passive-fed coform process. Therefore, only relevant meltblowing process parameters were studied; these included die-to-collector distance (DCD), vacuum pressure, die pressure, and converging angles.

Biax meltblowing spinnerets were used for all of the dual-beam (db) experiments. The gravity-fed experiments were done at Biax Fiber-Film Corporation in Appleton WI (BFC-db). These experiments represented the proof of concept, where a lawn spreader was used to introduce a free-fall curtain of model particles (MSGB and PAC) between the polymer streams (see Figure 7.2). Different convergence angles, DCDs, and vacuum pressures were tried; these include both vertical and angled filament streams (see Figure 7.7 and Figure 7.8).
The main trials with the shaker-chute assembly were done at The Nonwovens Institute (NWI-db), shown in Figure 7.3. Chapter 8 presents all the related details for these two sets of trials. This chapter only reviews the feasibility of passive-fed particle supply and all the data are related to control unloaded samples, unless otherwise mentioned.

Note: dies pressures were identical for each trial (top and bottom dies had the same pressure).
The first set of trials, conducted in September 2015 (Sep.2015), focused on understanding the process and investigating optimal coform parameters. These included effect of chute presence and chute position, effect of particle size, effect of dies pressures, effect of vacuum pressure, and effect of DCD. This set of trials suggested the optimal dies pressure, vacuum pressure, and chute position for the second set of trials. Figure 7.4 illustrates the configurations and process parameters for the Sep.2015 NWI-db coform trials.
Figure 7.4: NWI-db configuration and process parameters for the Sep.2015 coform trials

Table 7.2 demonstrates the DOE (design of experiments) and process parameters for unloaded control samples. Control samples provided information to examine the effect of incorporation means on web properties, shaker-chute presence in the converging volume.

Table 7.2: Process parameters for Sep.2015 control webs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chute Position (cm to top die)</th>
<th>Particle Feed Rate (g min⁻¹)</th>
<th>DCD (cm)</th>
<th>Air Pressure (psi)</th>
<th>Vacuum Pressure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control-8</td>
<td>NA</td>
<td>NA</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Control-9</td>
<td>NA</td>
<td>NA</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Control-10</td>
<td>NA</td>
<td>NA</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-0-8</td>
<td>Flush (0)</td>
<td>NA</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-0-9</td>
<td>Flush (0)</td>
<td>NA</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-0-10</td>
<td>Flush (0)</td>
<td>NA</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-f-8</td>
<td>Far (15.2)</td>
<td>NA</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-f-9</td>
<td>Far (15.2)</td>
<td>NA</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-f-10</td>
<td>Far (15.2)</td>
<td>NA</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-m-8</td>
<td>Middle (7.6)</td>
<td>NA</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-m-9</td>
<td>Middle (7.6)</td>
<td>NA</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Control-Ch-m-10</td>
<td>Middle (7.6)</td>
<td>NA</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
</tbody>
</table>
The second set of trials, conducted in February 2016 (Feb.2016), focused on studying particle loading limits and producing samples that allowed for establishing process-structure-property relationships. These included effects of particle feed rate and effects of streams converging point. Converging point can be modified by changing the DCD in the set coform configuration shown in Figure 7.4. Bottom and top streams converge before the drum for DCDs larger than 32 cm, and vice versa.

7.2.3 - Pressure Profile via Pitot Tube
As shown in Figure 7.5, top die, bottom die, and collecting drum create a "converging volume" wherein the shaker-chute would discharge AM particles. Understanding the pressure profile at different locations within the converging volume is critical; this was measured by a Pitot-static tube. Stable and viable discharge of gravity-fed particles in the converging volume is only possible at locations with not-positive dynamic pressures.

Figure 7.5: NWI-db converging volume

7.2.4 - Passive Particle Dispensing via Shaker-Chute
Eriez Hi-Vi vibratory feeder, model 46-C, was used to dispense AM particles. A Unicon N-12 vibratory controller was used to control the vibration frequency (feeding rate) from almost zero to 3000 Hertz. According to NWI-db configuration, a chute was required to direct the
model particles from the shaker to the converging volume. Figure 7.6 shows the vibratory feeder and the aluminum chute.

Figure 7.6: vibratory feeder and the aluminum chute (shaker-chute)

Prior to Sep.2015 coform trials with the shaker-chute assembly, the following parameters were investigated to assure the applicability and efficiency of such system:

- Perturbation of fiber/web formation process in presence of a foreign object in the converging volume;
- Requirements for continuous and uniform overall flow over time;
- Available discharge rates (and related setting on the shaker);
- Flow uniformity across the width.

The first parameter, web formation perturbation, was investigated through CFD simulations and some experiments (see 7.4.2 - for details).

Regarding the continuous and uniform overall flow, the parameters that determine the flowability of gravity discharge in inclined chutes include:

- Particle/powder properties: density, size, shape, roughness, surface friction, electrical properties, moisture, homogeneity, interparticle properties, etc.;
Intrinsic properties: temperature and relative humidity;

External factors: feeding rate (and vibration), chute design (dimensions and incline angle)

Mutual factors: chute-particle composition, coefficient of friction between the two [492-497].

From the above factors, we had control over particle size, feeding rate, chute angle, and chute surface friction. In general, smaller particles (< 250 µm) show more complex flow behavior and have larger angle of repose. Therefore, the flowability was investigated at different particle sizes, chute angles, feeding rates, and chute surface finishes.

The first step was to create a slick surface (low coefficient of friction) on the aluminum chute.

Secondly, the relationship between chute angle and particle size was investigated. As mentioned before, smaller particles flow on steeper inclines. Uniform webs are achievable on NWI-db when the angle of inclined Biax die (top die in Figure 7.4) is larger than 32°.

Once the flow continuity was confirmed, the discharge uniformity over time was studied. To do so, the discharge was weighed with respect to time. This was done at chute angle of ~ 22°, different vibration frequencies, and three particle sizes (AM-425, AM-710, and AM-850).

Last but not least, the discharge uniformity across the width was investigated by using a vial holder with separated slots shown in Figure 7.20.a. Chute angle was ~ 22°, frequency was 3 Hz, ground AM size was 425 – 710 µm (AM-425), and 5 measurements were done. Discharge uniformity across the width was also confirmed with slow-motion video recording/observations.
7.3 - CFD SIMULATIONS

ANSYS Fluent 14.5 was used to simulate the pressure profile and velocity contours in the converging volume. To simplify the solution, in both of the cases, the effect of polymer and high process temperature were neglected, i.e. room-temperature air was the only present fluid. The top and bottom dies were the inlets and the open area on the collecting drum was the outlet. Meshing size modification and meshing refinement were applied to optimize the solution time. All of the geometry dimensions were based on the actual configuration and solutions were based on steady state (disregarded the transient state upon the start of meltblowing and relied on the steady state throughout the process).

Boundary conditions were chosen based on the desired output. For the pressure profile case, the inlet boundary conditions were the measured air pressures during the process. For the velocity contours case, the inlet boundary conditions were the calculated air velocities at the dies exits. The outlet boundary condition for both of the cases was zero gauge pressure.

7.4 - RESULTS AND DISCUSSIONS

7.4.1 - Proof of Concept at BFC-db

In the vertical BFC-db coform, the adhesion between the web layers was poor and they could not contain the PAC particles (see Figure 7.7). The second polymer stream, the left one, laid on the rather-solidified first polymer stream/web and filaments did not have the chance to intermingle with each other. In addition, presence of PAC particles on the first base web interfered with potential bonding between the two webs. Not only PAC particles did not come into the filaments, but also they contributed to web’s delamination.
However, angled-streams configuration showed successful particle incorporation. Free-falling PAC particles and angled polymer streams had the opportunity to comingle and intermingle with each other before they lay on the collecting belt. Figure 7.8 shows related process conditions and the resulted hybrid web.
Figure 7.8: Angled BFC-db configuration and resulting hybrid web

Coform trials using the gravity-fed lawn spreader were successful in the angled BFC-db. This suggested that small particles (< 200 µm) could be introduced in between the filament streams in a free-fall fashion. Basis weight of the control web was around 75 g m⁻² and basis weight of hybrid PAC-NW web was around 91 g m⁻²; which translates to a PAC composition of 18% by mass. Since the discharge uniformity and rate of the lawn spreader were poorly controllable, the produced hybrid webs were not characterized any further. It was concluded
that angled dual-beam coform process was a promising technique to incorporate particles without any controlled airflow.

7.4.2 - Discharge Feasibility in Converging Volume

Figure 7.9 shows the pressure profile in the converging volume. Based on the CFD simulations, the gauge pressure was smaller than $2 \times 10^{-9}$ Pascal, where the distance was more than 5 cm away from either of the air streams.

Figure 7.9: Pressure profile in the converging volume, simulated by ANSYS Fluent (no heat, no polymer)

Pitot-static tube measurements confirmed the simulation results. Readings were around zero kPa where the tube was held at 5+ cm distance from the air streams. Readings were positive and closer to the collecting drum (less than 10 cm).

Figure 7.10 demonstrates the velocity contours in the meltblowing zone. Each air stream created two vortices, a larger vortex outside of the converging volume and a smaller one
inside of the converging volume. The interior vortices merged into one another at a point that is around 15 cm away from the die blocks, suggesting more turbulent air motions at this point.

Based on these results, the turbulent location and the vortices magnitude can be regulated by adjusting the air pressures of each die and by adjusting the vacuum pressure. This was not the focus of this research, and can be simulated and optimized in future studies.

To study the potential perturbation, a model cardboard sheet was placed in the converging volume while the MB process was running. The size of the sheet was that of the chute, 1/4"-thick and 4"-wide. No perturbation was visible to the naked eye unless the sheet would pass more than 20 cm past the die blocks (see Figure 7.11).
It was concluded that AM particles could be dispensed in the converging volume provided:

- The discharge location was more than 5 cm away from either of the meltblowing streams; and
- The chute discharge was located less than 15 cm away from either of the die blocks.

Figure 7.12 illustrates three images from Sep.2015 hybridization trials at Flush (0 cm), Middle (7.6 cm), and Far (15.2 cm) chute locations for AM-425.
It was observed that the shaker-chute assembly could dispense AM-425 particles in the converging volume only based on the force of gravity; no particle waste was observed. Figure 7.12 also shows where the particles entrained the filament streams, "entrainment zone".

**7.4.3 - Influence of Chute Presence on Web Properties**

Figure 7.13 shows the basis weight and basis weight uniformity of Sep.2015 unloaded webs.
Basis weights of control webs

Basis Weight (g/m²)

Chute Position

NA    Flush    Middle    Far

(a)

8 psi    9 psi    10 psi
CV% of basis weight (across)

Chute position - Location across

(b) Basis weight CV %

- 10 psi
- 9 psi
- 8 psi

NA  Flush  Middle  Far
The presence of the chute in the converging volume did not have a significant effect on basis weight uniformity. The non-uniformity in the control webs in the absence of chute was inherent of the meltblowing process with no metering pump.

Figure 7.14 shows the average fiber diameter for Sep.2015 unloaded samples. Data is based on 600+ fiber diameter measurements from SEM micrographs on each side of the web. The top direction (W) shows the fibers from the Wayne extruder and the bottom direction (B) shows the fibers from the Biax extruder.
Figure 7.14: Average fiber diameter, measured on each side of the Sep.2015 unloaded web

Presence of the chute in the converging volume did not introduce a significant change to the average fiber diameter; that is desirable for this chapter’s purposes.

Filtration efficiency versus pressure drop of Sep.2015 unloaded webs is plotted in Figure 7.15. Results represent three measurements on PALAS filtration testing equipment, with a volumetric flow of 360 lpm through 100 cm² filter area (face velocity: 0.6 m s⁻¹).
No specific trend was observed in the filtration properties.

In general, it was concluded that the presence of the chute did not affect the nonwoven web properties. This was a significant parameter determining the successful hybridization technique using the shaker-chute assembly. Results were particularly important because none of the prior art has conducted (or reported) such "sanity check" on their process viability.

7.4.4 - Uniform Particle Supply via Shaker-Chute

Continuous and uniform overall flow

Three types of finishes were tried on the chute's surface; dry lubricant, food-grade silicone polish, and metal polish (see Figure 7.16). They all render the surface slick; but only the latter (NOXON metal polish) provided proper surface for continuous particle sliding. Dry lubricant and silicone polish caused greasy/charged surfaces that particles would stick to.
For the studied materials/conditions (AM and metal-polished aluminum), none of the ground AM slid down the chute when the angle was smaller than ~ 22°. Ground AM larger than 425 µm had uniform and continuous flow when chute was angled at > 22° (see Figure 7.17.a). Discontinued particle flow was observed in any of the following situations: not-finished surface, surface finished with dry lubricant or silicone polish, chute angled at < ~ 22°, particles smaller than 425 µm (see Figure 7.17.b).

Figure 7.17: Ground AM flow on the Al-chute: (a) continuous and (b) chute angle < ~ 22° or particle size < 425 µm

Figure 7.18 shows an instance of the chute discharge mass with respect to time for AM size 710 – 825 µm; graphs looked similar for all AM ≥ 425 µm. Measurements were done until before the balance weighing limit (~ 400 g) would reach.
Linear particle flow with respect to time was observed at all tested frequencies and for all particle sizes of ground AM. Frequency was controlled by the knob on Unicon control box; 0, 2.5, 5, 7.5, 10, 15, and 20% correspond to 3, 75, 150, 225, 300, 450, and 600 Hz, respectively.

*Available discharge rates*

The width of the opening on the shaker tray (see Figure 7.19.a) was modified to reach the reported discharge rates (see Figure 7.19.b). By modifying this opening, it was possible to reach desirable discharge rates. The lowest discharge rate with current settings was ~ 80 g min\(^{-1}\), and the highest discharge rate was ~ 2200 g min\(^{-1}\).
Flow uniformity across the width

Figure 7.20.a demonstrates the method that was used to measure flow uniformity across the width and Figure 7.20.b shows the results.

Figure 7.20: a) Vial holder used for studying width discharge uniformity, b) width discharge uniformity
The CV% of the discharged mass in 4 middle bins were smaller than 4%; this was a reasonable variation for our process; Figure 7.21 shows two screenshots of these videos.

![Screenshot of slow-motion videos from the shaker-chute](image1)  ![Screenshot of the chute slide](image2)

Figure 7.21: Screenshots of slow-motion videos form the shaker-chute: a) discharge slot, b) chute slide

It was concluded that the shaker-chute assembly is a promising particle dispenser for NWI-db coform process. This was based on flow continuity-uniformity and uniformity across the width.

From a practical perspective, these results are even more important since they suggest general guideline for investigating a viable incorporation means. The shaker-chute assembly was one of the modules of this chapter. However, the general procedure and action plans are translatable to future protocols to investigate process feasibility.

As mentioned in the Introduction, none of the prior arts reported the influence of particle incorporation means on the web formation process and web properties. Results suggest that extensive feasibility studies are required to verify that the incorporation technique does not adversely influence the web properties.

7.5 - CONCLUSIONS

This chapter focused on the feasibility of producing dual-beam coform webs via passive-feed particle incorporation. Free-falling PAC particles intermingled with filament polymer
streams in the angled BFC-db coform configuration (successful proof of concept). Particle
discharge feasibility in the NWI-db coform configuration was simulated and verified through
CFD modeling and Pitot-static tube measurements. Feasibility studies focused on pressure
profile and velocity contours in the converging volume. Basis weight uniformity, fiber
diameter measurements, and filtration properties did not change significantly in the presence
of the chute in the converging volume. The results suggested that gravity-fed AM particles
could entrain the polymer streams, and comingle with the filaments in NWI-db coform
process. Continuous and uniform overall flow and flow uniformity across the width was
confirmed for the shaker-chute particle supply means.

It was concluded that gravity-fed AM particles could be incorporated in nonwovens via
NWI-db coform process. The incorporation means was able to deliver a uniform particle
supply without introducing any negative impacts on the nonwoven web properties.
Procedures and results can be used as general guideline for investigating a viable
incorporation means.
CHAPTER 8: High-Surface-Area Coform Nonwovens: Structure-Process-Property Relationships
8.1 - INTRODUCTION
High-surface-area adsorptive nonwovens play an important role in many applications such as adsorption filtration-purification, energy-fuel storage, bio-separation, and odor removal. Functionality of such media is determined by several factors including:

- Adsorbent type: specific surface area, surface chemistry-functionality, adsorption affinity (energy), etc. (discussed in chapter 5);

- Operational conditions: temperature, humidity, pollutant(s) concentration(s), volumetric flow, etc. (discussed in chapter 4); and

- Structural parameters: amount of adsorbent materials (loading), available surface-pore area vs. covered (masked) areas, particle stability within the structure (shedding), structural tortuosity and thickness of the carrier and resulting residence time, packing density and pressure drop, distribution uniformity, etc.

Structural properties are highly dependent on the method used to incorporate the adsorbent in the nonwovens. The focus of this study is on coform incorporation methods and some of the resulting hybrid coform structural properties are mentioned here. Coform nonwovens with adsorbent loadings of 10% to 99% by mass of the composite medium (10 to 600 g m\(^{-2}\)) have been reported. These structures can retain 87% to 100% of their adsorbent particles in a typical shakeout test (shedding: 0% – 13%). Adhesives, adhesive polymers, and/or post-processes (such as lamination and heat-bonding) may be required to achieve such properties. Their pressure drop should comply with the respective application standard [245, 249, 468, 471, 472, 475, 484, 489, 491, 498-505].

Incorporation of adsorbents in coform nonwovens have been reported in the prior art. However, structure-process-property relationships for high-capacity low-pressure-drop non-shedding nonwovens were not well established. Non-shedding coform structures with high loadings (> 98%) of adsorbents that do not need adhesives and/or post-processes have not been reported. In addition, two important structural parameters have been overlooked in the
prior art, adsorbent distribution uniformity and adsorbent available (uncovered) surface-pore area.

This chapter focuses on establishing the structural parameters of hybrid adsorptive nonwovens produced by the NWI-db coform process. A brief review of NWI-db coform configuration, hybridization parameters, and testing protocols are presented. Results can be used as guidelines for understanding structure-process-property relationships of hybrid adsorptive nonwovens. These include adsorbent distribution uniformity, media air permeability and filtration properties, thickness and microstructure, shedding (adsorbent stability), and BET surface area analysis.

8.2 - MATERIALS AND METHODS
8.2.1 - Polymer and Model Particle
Polypropylene (melt flow index 30) was used for all experiments. Ground Ammonasorb AC (AM) was used to accomplish the coform trials and to produce hybrid adsorptive nonwovens (see Table 7.1 for size ranges). Two different batches of AM were ground for each trial (AM-15 for Sep.2015 trials and AM-16 for Feb.2016 trials); this was important for the microporosity analyses and was taken into consideration (see Table 8.3).

8.2.2 - NWI Dual-Beam Coform
Two major trials were accomplished. The first set of trials, conducted in Sep.2015, focused on understanding the process and investigating optimal coform parameters. These included effect of chute position, effect of particle size, effect of dies pressures, effect of vacuum pressure, and effect of DCD (die to collector distance). This set of trials suggested the optimal dies pressure, vacuum pressure, and chute position for the second set of trials. Figure 7.4 illustrates the configurations and process parameters for the Sep.2015 NWI-db coform trials.
The second set of trials, conducted in Feb. 2016, focused on studying particle loading limits and producing samples that allowed for establishing process-structure- property relationships. These included effects of particle feed rate and effects of streams converging point. Converging point can be modified by changing the DCD; bottom and top streams converge before the drum for DCDs larger than 32 cm, and vice versa (see Figure 8.1). Three Feb.2016 coform configurations were labeled as CAD-27 (converging after drum for the DCD of 27 cm), C@D-32 (converging at drum for the DCD of 32 cm), and CBD-37 (converging before drum for the DCD of 37 cm).

Note: dies pressures were identical for each trial (top and bottom dies had the same pressure).

8.2.3 - Hybridization Parameters

These parameters were categorized into two groups, meltblowing parameters and particle-incorporation parameters. To understand the interactions between meltblowing process
parameters and hybridization process, different dies air pressures, vacuum pressure (%), and DCDs were investigated. Available model particles (AM) and incorporation means (shaker-chute) allowed for studying following particle-incorporation parameters, chute position, particle feed rate, and particle size. Table 8.1 demonstrates the DOE (design of experiments) Sep.2015 trial plan for initial hybrid samples (control unloaded webs are discussed in chapter 7).

Table 8.1: DOE of Sep.2015 hybridization trial

<table>
<thead>
<tr>
<th>Code</th>
<th>Chute Position (cm to top die)</th>
<th>Particle Size (µm)</th>
<th>Feed Rate (g min⁻¹)</th>
<th>DCD (cm)</th>
<th>Air Pressure (psi)</th>
<th>Vacuum Pressure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hy-0-S-2.5-30-8-80</td>
<td>Flush (0)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Hy-0-S-2.5-30-9-80</td>
<td>Flush (0)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Hy-0-S-2.5-30-10-80</td>
<td>Flush (0)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Hy-m-S-2.5-30-8-80</td>
<td>Middle (7.6)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Hy-m-S-2.5-30-9-80</td>
<td>Middle (7.6)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Hy-m-S-2.5-30-10-80</td>
<td>Middle (7.6)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Hy-f-S-2.5-30-8-80</td>
<td>Far (15.2)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>8</td>
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</tr>
<tr>
<td>Hy-f-S-2.5-30-9-80</td>
<td>Far (15.2)</td>
<td>425</td>
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<td>80</td>
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<tr>
<td>Hy-f-S-2.5-30-10-80</td>
<td>Far (15.2)</td>
<td>425</td>
<td>74</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Hy-0-S-7.5-27-9-100</td>
<td>Flush (0)</td>
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<td>98</td>
<td>27</td>
<td>9</td>
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</tr>
<tr>
<td>Hy-m-S-7.5-30-8-80</td>
<td>Middle (7.6)</td>
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<td>98</td>
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<tr>
<td>Hy-m-S-2.5-27-10-100</td>
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<td>27</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Hy-f-S-2.5-27-8-100</td>
<td>Far (15.2)</td>
<td>425</td>
<td>74</td>
<td>27</td>
<td>8</td>
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<tr>
<td>Hy-f-M-7.5-30-10-100</td>
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<tr>
<td>Hy-f-M-5-30-9-80</td>
<td>Far (15.2)</td>
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<tr>
<td>Hy-m-M-5-27-9-80</td>
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<tr>
<td>Hy-m-M-5-30-9-100</td>
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<tr>
<td>Hy-0-M-2.5-27-8-80</td>
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<td>80</td>
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<tr>
<td>Hy-0-M-5-27-9-100</td>
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<td>100</td>
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<td>Hy-0-L-5-30-8-100</td>
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<tr>
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<td>98</td>
<td>30</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Hy-m-L-2.5-27-10-100</td>
<td>Middle (7.6)</td>
<td>850</td>
<td>74</td>
<td>27</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Hy-m-L-7.5-30-8-80</td>
<td>Middle (7.6)</td>
<td>850</td>
<td>98</td>
<td>30</td>
<td>8</td>
<td>80</td>
</tr>
<tr>
<td>Hy-f-L-2.5-30-9-80</td>
<td>Far (15.2)</td>
<td>850</td>
<td>74</td>
<td>30</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>Hy-f-L-7.5-27-8-100</td>
<td>Far (15.2)</td>
<td>850</td>
<td>98</td>
<td>27</td>
<td>8</td>
<td>100</td>
</tr>
</tbody>
</table>
Sep. 2015 trials helped establish optimal dies pressures, vacuum pressure, and chute position. Feb. 2016 trial plans were geared to develop high-loading non-shedding hybrid nonwovens. DOE of Feb. 2016 trials are presented in Table 8.2.

Table 8.2: DOE of Feb. 2016 hybridization trial

<table>
<thead>
<tr>
<th>Code</th>
<th>Feed Rate (g min⁻¹)</th>
<th>DCD (cm)</th>
<th>Particle Size (µm)</th>
<th>Chute (cm to top die)</th>
<th>Air Pressure (psi)</th>
<th>Vacuum Pressure (%)</th>
</tr>
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<td>32</td>
<td>NA</td>
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<td>32</td>
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<td>8</td>
<td>100</td>
</tr>
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<td>330</td>
<td>32</td>
<td>425</td>
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</tr>
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<td>32</td>
<td>425</td>
<td>3</td>
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<td>100</td>
</tr>
<tr>
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<td>425</td>
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</tr>
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<td>C@D-32-765</td>
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<td>CAD-27-475</td>
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<td>CAD-27-581</td>
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<tr>
<td>CAD-27-1100</td>
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<td>27</td>
<td>425</td>
<td>3</td>
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</tr>
<tr>
<td>CAD-27-1490</td>
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<td>CAD-27-1720</td>
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<td>425</td>
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<td>NA</td>
<td>37</td>
<td>NA</td>
<td>3</td>
<td>8</td>
<td>100</td>
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<tr>
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<td>119</td>
<td>37</td>
<td>425</td>
<td>3</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>CBD-37-328</td>
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<td>37</td>
<td>425</td>
<td>3</td>
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<td>100</td>
</tr>
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<td>37</td>
<td>425</td>
<td>3</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>CBD-37-577</td>
<td>577</td>
<td>37</td>
<td>425</td>
<td>3</td>
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<td>CBD-37-773</td>
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</tr>
<tr>
<td>AM-710-27-1460</td>
<td>1460</td>
<td>27</td>
<td>710</td>
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<td>AM-710-32-1460</td>
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<td>32</td>
<td>710</td>
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<tr>
<td>AM-710-37-1460</td>
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<td>37</td>
<td>710</td>
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<td>32</td>
<td>300</td>
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<td>710</td>
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<tr>
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<td>32</td>
<td>850</td>
<td>3</td>
<td>8</td>
<td>100</td>
</tr>
</tbody>
</table>
The CBD-37 samples were not produced because of the limited amount of AM-425. The last six samples were produced to explore the process boundaries (particle size and loading). Therefore, analytical measurements and discussions were not applicable for these samples.

8.2.4 - Analytical Instruments and Protocols

- Basis weight and loading measurements

Basis weight measurements were done to examine particle loading, particle distribution uniformity, web uniformity across and along, and degree of potential edge effect(s). The latter was determined for Sep.2015 hybrid webs and sampling protocol was modified accordingly for Feb.2016 samples. Figure 8.2 illustrates the sampling protocols for the above samples.

Figure 8.2: Sampling protocols for Sep.2015 and Feb.2016 hybrid nonwovens
The results are an average of ten measurements and expressed in two ways, **AC loading gsm** (grams of AM particles in one m$^2$ of the hybrid nonwoven) and **AC loading%** (mass ratio of AM particles to hybrid nonwoven). A commercial benchmark (CBM) was used for comparison.

- **Thickness**

Thickness was investigated based on ASTM – D5729 (anvil pressure of 0.6 psi) and results represent the average of five measurements. This test was done to understand how AM particles settle in the nonwoven structure based on specific process parameters.

- **Fiber diameter**

Fiber diameter measurements were obtained from SEM micrographs via ImageJ software. Results are based on 600+ measurements from 10+ images. This test was done to study the impact of DCD and particle loading on fiber diameter distribution (based on the visible fibers on each side of the fabric). The bottom side of the web was labeled as "B" (Biax extruder) and the top side of the web was labeled as "W" (Wayne extruder).

- **Shedding**

Particle stability, structural durability, particle retainability, particle release, particle shake-out, or shedding are some common terminologies in the literature that refer to a similar concept. This important structural characteristic determines how well the particles are attached, intermixed, or comingled with the fibrous component. Therefore, a testing protocol was developed and conducted to examine NWI-db's coform technology platform.

Typically, the hybrid nonwoven is affixed to a mesh sieve and shaken for a period; the ratio of the mass of released particles to the original sample mass is defined as shedding or shake-out. Important parameters are affixation method, sample size, shaking pattern, and shaking time (5 – 10 minutes) [167, 168, 481, 506-510].
Figure 8.3 demonstrates the testing protocol, where seven 5cm×5cm samples are pinned down to a US mesh #10 (2mm). The Tyler Ro-Tap RX-29 instrument was used to shake the samples until shedding stopped (oscillations per minute: 285, oscillations displacement: 1.1cm×2.9cm, taps per minute: 150, hammer weight: 2.5 kg). The amount of shake-out was measured every minute until there was no measurable amount (0.1 mg resolution). Tapping elevated the samples from the mesh sieve, so particles could shed from all six sides of the sample. Zero (or minimal) area coverage and extended shake-out tests ensured vigorous shaking conditions.

The results are expressed in two ways, total shedding (shedding throughout the test duration) and residual shedding (total shedding minus shedding in the first minute). It was assumed that the shedding in the first minute was from the cut edges. Shedding half-decay times are presented as well; this is the time it takes for shedding to be reduced by one half. Our extended shake-out test (shake until it stops) enables future comparisons between our results and other results (where shaking is only for a defined period).

➢  Filtration properties

The results represent three measurements on PALAS filtration testing equipment, with a volumetric flow of 360 lpm through 100 cm² filter area (face velocity: 0.6 m s⁻¹). This test was done to determine if the addition of AM particles to unloaded nonwovens would have
adverse impacts on the filtration properties (i.e. increase in pressure drop and/or decrease in filtration efficiency). Filtration properties studies were only applicable to Sep.2015 samples. Feb.2016 samples were so thick that the instrument could not seal the air duct.

- **Air permeability**

The air permeability of the samples was measured by TextTest FX-3300 instrument. The test area was 20 cm² and results are averages of 10 measurements. This test was done for Feb.2016 samples to understand the effect of high loading/packing of AM particles in hybrid nonwovens. The goal was to investigate if particle addition and loading would adversely decrease the media air permeability.

- **Microporosity and BET surface area analyses**

NWI’s ASiQ instrument (from Quantachrome, Boynton Beach, FL) was used to analyze the surface area and pore characteristics of samples. This test was done to examine the uncovered surface-pore areas. Microporosity analysis data included BET specific surface area (SSA_BET), total pore volume (V_t), volume of mesopores (V_meso), volume of micropores (V_mic), and micropore contribution (V_mic/V_t).

The outgassing protocol and analysis parameters (relative pressure point measurements) were constant for all samples (two replicates per test). It was critical to establish the optimal outgassing (baking) temperature-duration that is applicable for both adsorbent samples and hybrid nonwoven samples. Based on a literature cross-check, temperature range of 90°C to 150°C for 6 hours was the most common baking temperature-duration [24, 441, 443, 452, 455, 461, 462]. To choose the "safe" baking temperature for the PP nonwoven carrier, fabric samples were baked at 90, 100, 110, 120, 130, 140, and 150°C for 6 hours. Structural changes were monitored by air permeability measurements and SEM micrographs. There was no significant structural transformation, or fiber fusing effect due to baking temperature, observable in SEM micrographs and/or air permeability measurements. However, warping occurred in samples baked at ≥ 120°C; see Figure 8.4.
The following common outgassing protocol (with ramps of 2°C min$^{-1}$) was established and used for all the tests:

60°C for 30 min $\rightarrow$ 80°C for 30 min $\rightarrow$ 100°C for 30 min $\rightarrow$ 110°C for 6 hours.

8.3 - RESULTS AND DISCUSSIONS

Process-structure-property relationships are mostly based on Feb.2016 hybrid nonwovens. A commercial cabin air filter was used as a benchmark (CBM); its structure was SB + MB + glue + AC + glue + SB (SB: spunbond and MB: meltblown). Concluding remarks are based on ANOVA tests (Duncan) at 95% confidence.

8.3.1 - Loadings and Basis Weight (Uniformity)

Figure 8.5 shows the average AC loading% for Sep.2015 samples. Two important observations were, lower loadings on the edges (A&E) for Flush and Middle samples, and uniform lower loadings across the Far specimens (widths: bottom die (B) = 15", Top die (W) = 5", chute = 4", specimens = 1").
The above observations indicated an edge effect in our coform configurations and determined the better chute positions (Flush and middle). In the Far chute position, particles encountered turbulent converging airflows as they exited the chute and comingled with the filaments over a wider span (> 5") (see Figure 8.6). However, in the Flush and Middle positions, particles comingled with the filaments within a narrower span.

Figure 8.5: Average AC loading% across Sep.2015 samples
Figure 8.6: Turbulent converging airflows in the Far chute position

Figure 8.7 presents the basis weight uniformity of Sep.2015 hybrid nonwovens.

![Graph showing basis weight uniformity](image)

(a) Basis weight CV%, hybrid webs-along
(b) Basis weight CV%, hybrid webs-across

Figure 8.7: Basis weight uniformity of Sep.2015 hybrid nonwovens: (a) along and (b) across

The middle chute position resulted in higher web uniformity, and lower die pressure (8 psi) caused less disturbance to the entraining AC particles (note: control unloaded webs with no
chute had 3 – 7% non-uniformity, inherent in a meltblowing process without a metering pump).

Therefore, in Feb. 2016 trials were done at Middle chute position and 8-psi die pressure, aiming at recognizing structure-process limitations to high AC loadings. Structural limitation was defined as excessive particle waste after web production. Process limitation was defined as failure in meltblowing and/or web collection due to excess particle discharge mass. Figure 8.8.a shows a snapshot of high-loading coform process where particles fall on two rows of filaments of the bottom die, and comingle with bottom and top filaments (4 rows) as they move toward the collecting drum. A tray was used to collect the particle waste (see Figure 8.8.b).

Figure 8.8: Feb. 2016 high-loading coform: (a) process snapshot and (b) waste collection tray

Feb. 2016 AC loadings and particle waste during production are presented in Figure 8.9. Note: control unloaded webs were 43 g m\(^{-2}\) at CV\% = 1.8.
Figure 8.9: AC loadings (g m\(^{-2}\) and %) and waste during production, Feb.2016 hybrid webs (control webs: 43 g m\(^{-2}\), and CBM: commercial benchmark)

Hybrid nonwovens with 99% AC loading (~ 4,000 grams of AC comingled with 43 grams of filaments) were produced. Particle waste during the process was less than 2% at feed rates lower than 1900 g min\(^{-1}\).

Higher nominal feed rates did not interrupt the meltblowing process and particles entrained in the filament streams. However, they did not come mingle with the fibers well enough and the
web structure failed to contain them upon winding up, resulting in high particle wastes (6, 11, and 15%). Two rows of bottom filaments could not contain high mass of AC, and particles broke the structure open and shed from the web. Using more number of rows might help extend this boundary limit. Sampling of hybrid webs at higher nominal feed rates was not possible because of their unstable high-shedding structures.

Findings were important from three standpoints: (I) although high-loading coform sorptive nonwovens have been reported, the amount of waste during the process was not mentioned. (II) Coform sorptive nonwovens with a basis weight of ~ 4,000 g m\(^{-2}\) were never reported. (III) Hybrid webs produced in NWI-db coform had high uniformity (CV% < 3.8).

Note: higher loadings of C@D-32 and CBD-37 samples were not produced since the required amount of AM was not available.

8.3.2 - Thickness

Figure 8.10 demonstrates the thickness of Feb.2016 hybrid webs (same trend was observed in Sep.2015 samples).

![Figure 8.10: Thickness of hybrid nonwovens from Feb.2016](image-url)
The linear increase in the thickness indicates that AC particles stacked on top of each other in the web structure. The resulting particle packing density depends on the wind-up compression force.

An important observation was in the control unloaded samples where thickness decreased by increasing the DCD from 27 to 32 and to 37. Increasing the DCD creates the opportunity for filaments to converge and intermingle with each other before the drum and form thinner structures.

Thickness was comparable to the CBM which is important from the application standpoint.

8.3.3 - Fiber Diameter
Average fiber diameter of bottom (B) and top (W) extruders were 10 µm and 2 µm, respectively. Fiber diameter distributions that were visible on each side of Feb.2016 control webs are shown in Figure 8.11 and Figure 8.12.
Figure 8.11: Fiber diameter distribution from the bottom (B) side of unloaded webs: (a) CAD-27, (b) C@D-32, and (c) CBD-37 (y-axis: frequency)

Figure 8.12: Fiber diameter distribution from the bottom (B) side of unloaded webs: (a) CAD-27, (b) C@D-32, and (c) CBD-37 (y-axis: frequency)
The results show that at higher DCDs small (2-µm) top fibers (W) have more appearance on the bottom side of the web. This was explained by the intermingling effect discussed in 8.3.2. Higher degree of filament intermingling is a desirable factor for non-shedding coform webs. Larger (10-µm) bottom fibers (B) did not appear on the top side of the web at any DCD.

To investigate the influence of particle discharge between the fiber streams, fiber size distribution of hybrid CBD-37 nonwovens was measured. The goal was to examine if AC particles would interfere with the observed fiber intermingling in CBD-37 webs. Therefore, highest (97.9% - 2046 g m⁻²) and lowest (88.5% - 333 g m⁻²) AC loadings of CBD-37 samples were studied (Figure 8.13).

The presence of AC particles showed a significant influence on fiber diameter distribution. By increasing the AC loading, appearance of 2-µm top fibers (W) decreased and a new size range (3 to 6 µm) was introduced, bigger fibers at lower loadings and vice versa. A potential mechanism for such observation was explained by fiber-particle comingling effect. 10-µm
bottom fibers would loop around the dispensing particles, and be dragged (attenuated) more; more loading: more particle-looped fibers: more drag force: thinner B fibers.

Having two different fiber size distributions was a unique aspect of NWI-db coform webs, which was believed to have significant influence on the hybrid web properties.

8.3.4 - Macro and Microstructure
Panoramic SEM micrographs of the cross section of unloaded Feb.2016 nonwovens are shown in Figure 8.14.

![SEM micrograph of Feb.2016 unloaded webs – cross section](image)

Figure 8.14: SEM micrograph of Feb.2016 unloaded webs – cross section
SEM micrographs of Feb.2016 unloaded samples confirmed the intermingling effect that was observed in thickness and fiber size studies. The top side of the CBD-37 was a composite of smaller and bigger filaments.

Feb.2016 hybrid nonwovens had high degree of intermingling at all DCDs. They showed a multi-layered structure when trying to disintegrate them. They did not release AC particles that were mechanically entrapped in the structure. Figure 8.15 shows an example where a CAD-27 web was extended in the z-direction by hand; 0.4 grams of fibers could contain and hold on to 40 grams of particles with negligible shedding.

![Image of SEM micrographs of Feb.2016 hybrid nonwovens](image)

Figure 8.15: Feb.2016 hybrid webs and z-direction pull-on snapshot, CAD-27 (AC: 3887 g m⁻²)

Two panoramic SEM micrographs from Feb.2016 hybrid nonwovens cross sections are presented in Figure 8.16 and Figure 8.17. Images showed a similar structural effect and these are only examples; all other cross sectional SEM micrographs are in Appendix B.
Figure 8.16: SEM micrograph of Feb.2016 hybrid nonwovens – cross-section, CBD-37 (AC: 923 g m$^{-2}$)

Figure 8.17: SEM micrograph of Feb.2016 hybrid nonwovens – cross-section, C@D-32 (AC: 3043 g m$^{-2}$)
Gravity-fed AC particles entrained the polymer streams at lower relative velocities. This resulted in uniform particle comingling with 2+4 rows of bottom and top filaments, and created a unique multi-layered structure. Such multi-layered stable coform structures were never reported in prior art; cross sectional SEM micrograph of CBM is shown in Figure 8.18 for comparison.

Figure 8.18: SEM micrograph of CBM hybrid nonwovens – cross-section, (AC: 409 g m⁻²)

Note: assuming that there is no friction between the chute and particles are spherical, they exit the chute at ~ 3.5 m s⁻¹. Air velocity in a conventional meltblowing die at 7.6 cm from the die (Middle particle discharge location – Feb.2016) is between 40 to 70 m s⁻¹ [511, 512].

### 8.3.5 - Shedding

Sep.2015 hybrid webs did not release measurable amount of particles in the shake-out test. Total shedding and residual shedding for Feb.2016 hybrid nonwovens are presented in Figure 8.19 (residual shedding: total shedding minus shedding in the first minute).
Residual shedding was less than half of total shedding for almost all of the samples, suggesting that most of the shedding was due to the cut edges. The amount of residual shedding was monitored and measured every minute until it stopped and results are shown in Figure 8.20.
Shedding showed an exponential decrease over time and more than 80% of the total shedding was in the first three minutes. This stressed the effect of cut edges on shedding, especially in the CBM. To investigate the effect of structure on shedding, shedding decay rates were analyzed (see Figure 8.21).
By fitting exponential functions to shedding decay rates, shedding half-decay times were calculated for Feb.2016 hybrid webs (Figure 8.22). Shedding half-decay time of one minute means that shedding cuts by 50% in one minute.
Shedding half-decay times were shorter for C@D-32 and CBD-37 hybrid webs; these were nonwovens with higher degree of intermingling and particle comingling. Shedding half-decay time for the commercial benchmark (CBM) was three times longer than that of CAD-27 webs (with the same AC- g m\(^{-2}\) loading). CBM results indicated that not only particles closer to the edges shed but also more particles dislodged from other locations and shed from the edge.

Results showed that NWI-db coform webs had superior structural integrity compared to the CBM. Smaller shedding percentages and shorter shedding half-decay times were achievable because of the unique multi-layered structure of the produced coform webs. Noteworthily, this was achieved without the use of any adhesives, adhesive polymers, or post-processing. Coform structures in the prior art had higher particle shedding although adhesives and/or post-processes were applied.
8.3.6 - Filtration Efficiency and Pressure Drop

Filtration properties of hybrid nonwovens were compared to control unloaded nonwovens for Sep.2015 samples (Figure 8.23).

![Filtration Efficiency vs. Pressure Drop Graph](image)

Figure 8.23: Filtration efficiency vs. pressure drop of Sep.2015 nonwovens

Incorporating the AC particles in nonwovens did not have a significant effect on filtration efficiency (-5.4%). However, addition of particles opened up the structure and resulted in a desirable decrease in pressure drop (-16.6%).

Another important observation was that Sep.2015 hybrid nonwovens did not shed any particles caused by the filtration testing airflow (face velocity of 0.6 m s\(^{-1}\) for ~ 5 min).

8.3.7 - Air Permeability

Air permeability of Feb.2016 nonwovens was measured to study the effect of high loadings of AC particles in the structure permeability (Figure 8.24).
Comingled carbon particles resulted in an opener structure until 98.5% AC loading (3000 AC g m\(^{-2}\)). At higher AC loadings, particles packed closely in the structure and decreased the air permeability.

Initial addition of AC particles (up to 1000 g m\(^{-2}\)) increased the air permeability of Feb.2016 coform webs by around 20%. However, addition of AC particles and glue in the CBM webs resulted in 40% drop in air permeability.

### 8.3.8 - Microporosity and BET Surface Area Analyses

Table 8.3 demonstrates the microporosity characteristics of AM particles and hybrid webs. Note: different ground AM batches were used for Sep.2015 and Feb.2016 trials (AM.425.15 and AM.425.16).
Table 8.3: Microporosity analysis of AM particles and hybrid webs (Hy.15.Far: hybrid web of Sep.2015 at Far chute position)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. Pore Size (Å)</th>
<th>MP (%)</th>
<th>P.Vol (cc g(^{-1}))</th>
<th>Composite SSA (m(^{2}) g(^{-1}))</th>
<th>AM Loading%</th>
<th>Estimated AM SSA (m(^{2}) g(^{-1}))</th>
<th>Potentially covered portion</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM.425.16</td>
<td>8.13</td>
<td>97</td>
<td>0.35</td>
<td>870.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Hy.15.Flush</td>
<td>8.12</td>
<td>97</td>
<td>0.28</td>
<td>681.5</td>
<td>85.0</td>
<td>801.9</td>
<td>7.9%</td>
</tr>
<tr>
<td>Hy.15.Middle</td>
<td>8.12</td>
<td>97</td>
<td>0.29</td>
<td>705.4</td>
<td>85.0</td>
<td>830.0</td>
<td>4.6%</td>
</tr>
<tr>
<td>Hy.15.Far</td>
<td>8.10</td>
<td>97</td>
<td>0.24</td>
<td>597.5</td>
<td>72.5</td>
<td>824.3</td>
<td>5.3%</td>
</tr>
<tr>
<td>AM.425.15</td>
<td>8.27</td>
<td>96</td>
<td>0.27</td>
<td>653.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Hy.16.Middle</td>
<td>8.15</td>
<td>97</td>
<td>0.24</td>
<td>607.9</td>
<td>97.9</td>
<td>622.2</td>
<td>4.7%</td>
</tr>
</tbody>
</table>

Estimated surface-pore area coverage was higher at the Flush chute position because particles entrained the filaments streams where fibers were still rather tacky (not solidified). Polymer fused into AC particles pores at this point, creating some heat-bonded area/point contacts. Incorporation of particles at Middle chute position resulted in less than 5% estimated surface-pore area coverage, leaving the majority of pores available for adsorption.

Note: ammonia adsorption capacity of hybrid webs was not evaluated because of inconsistent adsorption capacity of Ammonasorb batches (inconsistency was confirmed via EDS elemental analysis and FTIR spectroscopy).

8.4 - CONCLUSIONS

This chapter focused on establishing the process-structure-property relationships of hybrid coform nonwovens. Two sets of hybrid nonwovens (Sep.2015 and Feb.2016) were produced and analyzed; variables included DCD, die air pressure, vacuum pressure, particle feed rate, and chute position. Sep.2015 hybrid webs, produced at Middle chute position (7.6 cm from die blocks) and 8-psi air pressure, showed higher basis weight uniformity and less than 5% surface-pore area coverage. Feb.2016 hybrid nonwovens were produced at the above conditions and effects of DCD and AC loading limits were investigated.
Larger DCDs (32 and 37 cm) let the fiber streams converge before the collection drum and produced intermingled web structures. This was verified by fiber diameter distributions where fibers from the top stream appeared on the bottom side of the web. These webs (C@D-32 and CBD-37) were thinner, and their hybrid nonwovens had multi-layered structures compared to CBM webs.

Hybrid nonwovens with 99.0% loading of activated carbon were achieved (~ 4,000 grams of AC in ~ 40 grams of nonwoven web). These were multi-layered stable structures with particle shedding of less than 0.7%, without the use of any adhesives, adhesive polymers, and/or post-processes. Half-decay time studies showed that shedding was primarily due to cut edges. In addition, SEM micrographs confirmed the unique multi-layered structure.

Hybrid webs were compared to a commercial cabin air filter and showed superior properties. Addition of AC particles in our coform process did not decrease the air permeability, which is critical to air filtration media.
CHAPTER 9: Overall Conclusions and Recommendation for Future Work
9.1 - SUMMARIES AND CONCLUSIONS

Hybrid sorptive nonwovens have a variety of applications and there are several technologies to manufacture them. Coform process is a one-step technique to produce such media at high throughputs. Coform webs are produced by incorporating functional materials (such as activated carbon – AC) in the web while filaments are meltblown. The concept of coform process was introduced in 1954 by DuPont, and has been modified and improved ever since by 3M and Kimberly-Clark. A careful review of the patent literature showed that the process-structure-property relationships for coform process and structures were not well established. This study aimed at developing such guideline by exploring the feasibility of a novel coform configuration, followed by investigating and evaluating its products properties. A technology platform for fabricating high-loading, low-pressure-drop, and non-shedding adsorptive nonwovens were developed. The observations that were made in each module of this research and corresponding conclusions are as follows:

State-of-the-art coform process/products

The prior art has reported coform webs where sorptive particles are incorporated into the web via active feeding systems, such as fluidized air-jet particles. Mass concentrations (loading) of 10 – 99% AC have been reported where particle shedding was 0 – 13%. This was achieved by using adhesives, adhesive polymers, and/or post-processes.

✓ There was no published information whether or not it is feasible to produce coform structures via passive particle supply, such as gravity-fed; it was not mentioned why passive systems would not be feasible either. Limited process control could be one of the reasons. Active particle supply (air-jet) and presence of incorporation means in the meltblowing zone could influence basic web properties; these effects were not established.

✓ Coform webs can be produced from two routes, introducing the particles to one fiber stream or to two fiber streams (single-beam vs. dual-beam). It was not reported why
and how single-beam would be different than dual-beam. In addition, interactions between number of beams and active feeding systems were not studied.

✓ Although high loadings (> 98%) of carbon particles have been applied, hybrid media with basis weight of 600+ g m⁻² were barely reported or investigated. This is despite the fact that commercial filter media with about 3000 g m⁻² of AC are produced, and obviously required. The lack of structural integrity of heavy hybrid nonwovens at such loadings could be a potential reason.

✓ A clear relationship between loading, shedding, materials, and processes was not present. A study of the microstructure would reveal the mechanism(s) by which particles are entrapped in the nonwoven, i.e. mechanical entrapment and/or point/area bonded.

✓ The number of available (uncovered) adsorption sites are critical to adsorptive nonwovens. There was no quantitative data establishing if, how, and why coform process would influence adsorption capacities of hybrid webs.

**Selection of model adsorbent for ammonia as our model gas**

Activated carbon, the most conventional adsorbent material, requires chemical impregnation and activation for adsorption of reactive gases like NH₃. Non-conventional adsorbents such as HKUST metal organic frameworks (MOF) offer higher NH₃ adsorption capacities compared to AC, but they are expensive and moisture-sensitive. HKUST, HKUST-AC composite, and Ammonasorb AC were examined.

✓ Addition of AC to HKUST did not show a synergic effect in decelerating its structural collapse process in humid conditions. This moisture sensitivity could be studied and solved but was out of the scope of this study.

✓ Ammonasorb (AM) was chosen as our model adsorbent because of its commercial availability. Impregnation consistency was examined by EDS and FTIR analyses,
where batches found to be inconsistent. Thus, hybrid webs were not tested for NH₃ adsorption capacity. Consistency should be verified for future particles before incorporating them into the nonwoven.

**Dynamic NH₃ adsorption test apparatus**

Industrially, this test consists of monitoring inlet and outlet concentrations via two gas chromatography units according to specific standards. Lab-scale studies use one hand-held electrochemical gas sensor, which its accuracy is lower than analytical methods and cause discrepancies between the results. A universal calibration protocol for two-unit gas sensors was proposed and effects of test settings and parameters in three replicates were investigated.

- Discrepancies in the literature were correlated to the detection delay (lag) of electrochemical sensors; this was solved by using two sensors. To calibrate them, the difference between their readings was monitored when the adsorbent bed was empty; this protocol can be used for other gas-adsorbent systems as well.

- Important test settings (temperature, humidity, residence time, and inlet [NH₃]) were adjustable and their influence on AM was studied. Water molecules competed for adsorption sites in humid conditions and decreased the NH₃ adsorption capacity by 73%. Longer residence times allowed for more effective chemical adsorption process and higher adsorption capacities. Higher inlet [NH₃] created higher relative pressure of ammonia molecules around the adsorption sites and resulted in higher capacities.

- Influence of AM aging, preparation, and particle size on adsorption capacity was investigated. Capacity of aged AM (left in controlled lab environment for 24 hours) dropped by 51% since some of the adsorption sites were exhausted. AM that was baked at 110°C for 3 hours showed higher capacity since more sites were available (vacated) for NH₃ adsorption. Grinding the AM granules did not show a significant drop in adsorption capacity; however, creation of too many non-impregnated areas in AM dust (< 75µm) decreased the capacity by 32%.
Feasibility of single-beam coform via passive-fed particle supply

Gravity-fed AC particles were introduced to a single-beam commercial meltblowing line. Use of a controlled environment in front of the meltblowing die was examined by a coform "control box". Both of these studies were done on Biax die spinnerets for the first time.

- Turbulent meltblowing airflow blew the gravity-fed AC powder off the web at the examined configurations. The vortices that are present on the sides of fiber stream did not let the powder entrain the flow. One potential reason could be the powder size (~70 µm) and it was hypothesized that larger granules would be able to overcome the turbulence and entrain the fiber stream.

- Several geometries of a coform control box were examined and the truncated pyramid (diverging towards the collector drum) was the least disturbing to the web formation process. Study of the basis weight revealed that the coform box did increase web non-uniformity, not desirable for coform webs. Two potential remedies could be introducing controlled airflows to the box environment and/or using some baffles inside the box to use the interior turbulence in a beneficiary fashion. This could/should be optimized by initial CFD modeling.

Feasibility of dual-beam coform via passive-fed particle supply

After modeling and studying the airflow interactions in the converging volume between two Biax meltblowing fiber streams, a shaker-chute was used to passively feed AM particle in this volume. Overall, and across, discharge flow uniformity was examined in the shaker-chute assembly. The influence of chute presence in the converging volume on web properties was investigated.

- ANSYS Fluent simulations showed that the pressure profile in the converging volume would allow for dispensing gravity-fed particles in there. This was also confirmed by experiments where presence of a foreign object (same size as the chute) in the converging volume did not show visible effects on fiber/web formation process. The
results suggest that understanding of the dual-beam meltblowing process (only meltblowing process, not coform) would be critical for future optimizations and modifications to both meltblowing and particle incorporation process. This should be investigated by initial CFD modeling.

✓ The particle discharge rate of the shaker-chute was investigated to verify uniform overall flow and available flow rates. This was successfully done by real-time weighing and monitoring the discharge amount. Across flow-uniformity was confirmed by measuring particle discharge at different widths of the chute and by slow motion video/image observations.

✓ The presence of the chute did not have significant effect on web formation process or fabric basis weight uniformity. Coform trials were conducted successfully to prove the concept and produce sample hybrid webs for further analysis.

Process-structure-property relationships of hybrid adsorptive nonwovens

Non-shedding hybrid media with uniform 99% mass concentration of AC were produced without the use of adhesives or post-processes. Results were compared to a commercial cabin air filter to understand the relationship between shedding and microstructure. Web uniformity, thickness, fiber diameter, SEM micrographs, shedding, filtration properties, and microporosity of hybrid nonwovens were analyzed.

✓ Hybrid webs with 99% loading of AC particles (~ 4,000 g m^-2) and high uniformity (CV% < 3.8) were produced at minimal (<2%) particle waste. At higher loadings, fibers did not handle the particles and AC opened up the structure and shed out upon web winding process. Potential remedy would be to use more than two rows of meltblown filaments on the bottom die.

✓ Thickness was influenced by changing the DCD. Three DCDs were investigated to study how fibers and particles intermingle and come mingle with each other, CAD-27 were fibers converge after the drum, C@D-32 where fibers converged at the drum,
and CBD-37 where fibers converged before the drum. C@D-32 and CBD-37 samples had lower thickness, which was representative of higher degree of intermingling.

✓ Fiber diameter studies showed the similar intermingling effect where smaller fibers intermingled and passed through the larger fibers and appeared on the other side of fabric.

✓ SEM micrographs showed a stable multi-layered structure that was never reported before. Particles were mechanically entrapped between several layers of filaments; this was present in all samples. It would be worthwhile to investigate the fiber size on sides of the hybrid samples.

✓ Shedding was lower than 2% for CAD-27 samples and lower than 0.7% for other samples. Shedding half-decay time revealed that most particles are shedding from the cut edges of the samples. Unlike the commercial benchmark, particles did not dislodge within the structure. It would be worthwhile to study shedding in samples with sealed edges.

✓ Addition of AC particles did not increase the pressure drop or decrease the air permeability of samples. At loadings higher than 3,000 g m\(^{-2}\), particles packed closer in the structure and slightly decreased the air permeability.

✓ Microporosity showed that ACs' surface-pore area was not covered, and fully available for adsorption. It also confirmed that particle attachment mechanism was mostly mechanical since the specific surface area of hybrid webs was only 4.6% lower than that of AC adsorbents.

*Overall, a technology platform for incorporation of functional materials in nonwovens was developed. Results have established guidelines for fabricating high-loading, low-pressure-drop, and non-shedding adsorptive nonwovens.*
9.2 - RECOMMENDATION FOR FUTURE WORK

Based on this study's results, two directions for the future of this research can be recommended.

**Establishing the influence of other process parameters**

*Biax meltblowing process:* It is necessary to study the single- and dual-beam meltblowing process parameters. These could include effects of die pressure, vacuum pressure, DCD, fiber size, converging angle and location, temperature, throughput, collecting belt, and their interactions. These should be done by initial CFD modeling and further analyzed with experiments, and it is critical to understand this process to allow for more comprehensive coform studies.

*Fluid behavior:* CFD modeling could be used to optimize air and fiber streams in the converging volume so that higher web uniformity is achievable. This can be done by adjusting die air pressures and vacuum pressure and/or by using baffles in the converging volume. One potential could be using such adjustments to further study the feasibility of particle incorporation in NWI's single beam meltblowing.

*Fiber effect:* fiber diameters and number of filament rows were important parameters. Loading limitations and shedding properties could be overcome and further improved by discharging particles on more than two rows. The effect of different fiber sizes should be studied to establish the relationship between shedding and particle-fiber size.

*Shedding:* final finished filter products are sealed media and it would be beneficial to study the shedding behavior in samples with sealed edges. This would allow for a better understanding of microstructure and particle dislodging behavior within the structure.

*Particle effect:* feasibility of incorporating smaller particle size (< 200 µm) in the gravity-fed system should be explored. Another potential is to study the effect of particle density and shape; the latter could include particles with higher length-to-diameter ratio (fibers). Would denser particles, such as zirconia, entrain the filament streams or fall through?
Adsorption capacity: ammonia adsorption capacity of hybrid nonwovens was not studied because of inconsistent Ammonasorb particles. It would be worthwhile to investigate the effect of coform structures on dynamic adsorption capacity. The developed test apparatus is capable of testing fabric samples in a coin bed configuration (diameter: 5 cm).

Developing innovative coform materials

Different materials have been reported for use in the coform process; however, these are mostly limited to wood pulp fibers and adsorbents, such as activated carbon.

Unconventional adsorbents, such as metal organic frameworks, offer a variety of separation, storage, catalysis, and sensing applications. Use of such materials in scalable processes has been limited due to their price and operational sensitivity. Recently, more stable and moisture-insensitive MOFs have been reported in the literature. Would high throughput coform process increase the demand and drive the cost down?

Other than synthetic materials, living microorganisms and cells could be used in coform materials, opening the doors to a new generation of mass-produced bio-based functional materials. Could we use bio-waste to harvest energy in a large scale?!
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APPENDICES
Appendix A
Dynamic Adsorption Test Apparatus: Calibration and User Guide

1. Technical specifications

- **Dry air**: RH: 10 % ±5 %;
- **Ammonia**: 2030 ppm NH₃ balanced in nitrogen;
- **Needle Valve** [V.1]: default valve inside the chemical hood for the house air;
- **Diaphragm Valve** [V.2-6]: stainless steel, quarter-turn, self-venting valves (flow coefficient (Cᵥ): 0.14), working pressure of 3500 psi @ 20 °C;
- Single-stage regulator: pressure-reducing regulator with maximum inlet pressure of 1500 psi and maximum outlet pressure of 30 psi;
- **Dual-stage regulators**: stainless steel, four-port, dual-stage, self-venting regulators (Cᵥ: 0.1) with maximum inlet pressure of 3000 psi and maximum outlet pressure of 50 psi;
- **Rotameters** [R.1-4]: Variable-Area ball-floating flowmeter, Glass Tube, maximum inlet pressure of 145 psi, measured flow range of R.1 and R.2: 13 – 130 ml min⁻¹, R.3: 11 – 110 ml min⁻¹, R.4: 10 – 500 ml min⁻¹;
- **Humidity sensor**: touch-screen hand-held humidity indicator with a 10-feet probe extension cable and replaceable sensor. Operating conditions of: temperature range: -18 – 50 °C, humidity range (RH%): 0 – 95%, dew point range (DP): -30 – 50 °C;
- **Digital flow indicator**: positive-displacement (PD) volumetric flow calibrator, accurate and independent of the gas type, flow range of 50 – 5000 ml min⁻¹, operating pressure of
15 psi, non-condensing ambient humidity of 0 – 70 %, reading style: continuous, with user-selectable averaging function from 1 to 100 measurements, approximate time per reading: 1 – 15 seconds;

- **Ammonia detector** [D.1 and D.2]: electrochemical sensor-equipped detector, ambient pressure and temperature in 0 – 95% non-condensing humidity, detection range of 1 – 500 ppm ammonia with the resolution of 1 ppm, full response time of at least 2 minutes depending on the inlet NH₃ concentration/flow rate, "calibration" is required after each test, it takes 5 – 30 minutes for the detector to go down to "zero mode" after each exposure (depending on the exposure concentration/duration).

### 2. Calibration procedure

For all the following measurements, the outlet pressure on each regulator was set at 15 psi.

**Temperature and humidity:**

There were two different test conditions: humid test (with application of the bubbler) and dry test (when the bubbler is disconnected from the system). It was found that it takes 20 – 30 minutes for the temperature and humidity to stabilize once the user chooses the desirable settings on the regulators and rotameters; so this step should be done prior to each experiment. After 30 minutes, the change in the temperature is ±1 °C and the change in humidity is ±5 %, which are included in the test conditions.

#### 2.1. Flow rates

Each flow meter was connected to the digital flow indicator individually and it was found that R.1, 2, & 3 were showing 10 – 15% less flow rate. As shown in the schematic, R.1, 2, & 3 are all connected to R.4 to make up the mixed diluted test stream. When the three first rotameters (R.1-3) are adjusted to the desired flow rates and the knob on R.4 is fully open, it was found that R.4 shows 40 – 60% higher values. So, for accurate results, application of the digital flow indicator before the adsorbent bed is necessary while running the actual tests.

#### 2.2. Influent concentration setup

Since the ammonia sensors detect concentrations less than 500 ppm, a gas chromatography (GC) mass spectroscopy unit was used to find the right rotameters settings. Pure carbon monoxide (CO) was diluted as a model pollutant and the concentration was measured using the GC unit.

##### 2.2.1. Model pollutant

For each rotameter setting, diluted CO stream was passed through the system for 20 minutes to purge the line with the desired concentration. After that, 4 measurements were done within 15-min runs, one every 5 minutes. These measurements were done in three consecutive days to assess the precision. Table 1 shows the expected CO concentration versus the actual GC measurements for the following rotameter settings:

- 20% ~ R.1: 120 ml min⁻¹, R.2: 120 ml min⁻¹, R.3: 60 ml min⁻¹;
- 33% ~ R.1: 100 ml min⁻¹, R.2: 100 ml min⁻¹, R.3: 10 ml min⁻¹;
- 50% ~ R.1: 100 ml min⁻¹, R.2: 0 ml min⁻¹, R.3: 100 ml min⁻¹;
20% ~ R.1: 80 ml min\(^{-1}\), R.2: 80 ml min\(^{-1}\), R.3: 40 ml min\(^{-1}\);
14.3% ~ R.1: 120 ml min\(^{-1}\), R.2: 120 ml min\(^{-1}\), R.3: 40 ml min\(^{-1}\).

Table 1: Expected CO concentration versus the actual GC measurements

<table>
<thead>
<tr>
<th>Rotameter nominal dilution setting [CO]</th>
<th>Actual [CO]-[CV%] Day 1</th>
<th>Actual [CO]-[CV%] Day 2</th>
<th>Actual [CO]-[CV%] Day 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>25.25% --- (0.33%)</td>
<td>20.30% --- (0.73%)</td>
<td>23.41% --- (2.56%)</td>
</tr>
<tr>
<td>33%</td>
<td>36.54% --- (2.41%)</td>
<td>33.69% --- (0.89%)</td>
<td>36.03% --- (3.23%)</td>
</tr>
<tr>
<td>50%</td>
<td>48.86% --- (0.51%)</td>
<td>50.09% --- (2.13%)</td>
<td>54.32% --- (3.60%)</td>
</tr>
<tr>
<td>20%</td>
<td>26.58% --- (2.76%)</td>
<td>25.18% --- (2.81%)</td>
<td>24.08% --- (3.58%)</td>
</tr>
<tr>
<td>14.3%</td>
<td>19.08% --- (2.46%)</td>
<td>19.83% --- (3.74%)</td>
<td>19.20% --- (0.66%)</td>
</tr>
</tbody>
</table>

2.2.2. Ammonia
As it can be seen in the schematic, concentration of ammonia is measured before and after the adsorbent bed to determine the adsorption capacity. Since the maximum detection range of the sensor is 500 ppm, we will challenge the adsorbent bed with known concentrations of 450±50 ppm; this is analogous to dilution rate of 20% as the source ammonia is 2030 ppm. According to Table 1, the last rotameter setting yields the closest actual dilution rate to 20%. Factoring in that the molecular mass of ammonia is half that of CO, the following setup yielded the desired mixture:
R.1: 120 ml min\(^{-1}\), R.2: 120 ml min\(^{-1}\), R.3: 20 ml min\(^{-1}\).

The setting was applied in two consecutive days and two test conditions:
*Dry test* (T: 21 ±1°C, RH: 24 ±2%, and DP: 2 ±2°C), and
*Humid test* (T: 22 ±0.5°C, RH: 44 ±2%, and DP: 9 ±1.5°C).

Figure 1 shows the ammonia readings for the above conditions/settings. Table 2 demonstrates the average of actual readings up to 80 ppm.
Figure 1: Ammonia readings in 2 days, dry and humid conditions

Table 2: Average trend for the actual readings up to 80 ppm

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
<th>22</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Readings (ppm)</td>
<td>0</td>
<td>2</td>
<td>7</td>
<td>13</td>
<td>19</td>
<td>29</td>
<td>40</td>
<td>50</td>
<td>59</td>
<td>67</td>
<td>74</td>
<td>80</td>
</tr>
</tbody>
</table>

The variations in the influent concentration in different days explain the necessity of having two detectors. Accurate results can be obtained when the right settings are chosen; these are discussed in detail in the operation section.

3. Step-by-step Operation

1. Check all the connections and make sure they are all hand-tight and they follow the path according to the schematic.
2. Make sure the chambers for the bubbler and D.1 are not leaking. To check the bubbler, you can run the house air - open V.1 and V.2 and set the regulator at 15 psi delivery pressure - and check if you can get the maximum flow on R.1 (130 ml min⁻¹). To check the chamber for D.1, replace the bubbler with D.1 chamber (D.1 should be in the chamber) and follow the same procedure. Once you check the chambers do not open the lids.
3. Fill up the water bath with tap water and set the temperature at 25°C (check the temperature with a thermometer as well).
4. Set the digital flow indicator to present the average flow of 100 measurements.
5. Disconnect D.2 and adsorbent bed from the system and keep them outside of the hood until you are ready for the actual adsorption experiment.
6. Except for V.6 (labeled as "bed"), open all other valves on the control panel (V.2 – 5).
7. Open the main valves on the cylinders (1 turn) and the house air valve (1/2 turn) on the chemical hood (V.1).
8. Adjust all the regulators to deliver the gases at pressure of 15 psi.
9. Adjust the knobs on the rotameters to get R.1: 120 ml min\(^{-1}\), R.2: 120 ml min\(^{-1}\), R.3: 20 ml min\(^{-1}\) and keep R.4 fully open.
10. Let the system run for 30 – 40 minutes and then clear the min/max on the humidity sensor.
11. While the system is running, initiate the detectors by zeroing and "bump" testing as instructed in detector's manual.
12. After clearing min/max on the humidity sensor, connect D.1 to the end of bypass line and monitor the readings. It would take 8 – 12 minutes for the concentration to reach its highest stabilized value; the average of these readings should be 400 – 490 ppm.
13. Disconnect D.1 from the bypass line and connect it to the house airflow of the next chemical hood; this would shorten the time required for the sensor to go back to "zero". It would take around 5 minutes for the sensor to go down to ~ 50 ppm.
14. Weigh the bed (W1), weigh the NW pieces which you would be using to trap the particles (W2). Weigh the adsorbent material which is enough for your experiment and them transfer it to the bed. Weigh the loaded bed (W3). The weight of the test material is (Wa=W3-W1-W2).
15. To start the actual experiment now, connect the (preconditioned) loaded adsorbent bed, D.2, and D.1 back to the line as shown in the schematic.
16. At the same time, shut off V.5 and open up V.6 on the control panel. Record the average measurements of the flow from the digital flow indicator.
17. Continue the experiment until the readings on D.2 equals/exceeds the readings on D.1. Shut down V.4 now to collect the desorption data; and stop the experiment once you read 35 ppm on D.2.
18. Report the minimum and maximum for T (°F), RH (%), and DP (°F). Report the mass and volume of the adsorbent material and any preconditioning parameters. Report the average flow rate.
19. Generate the influent/effluent concentration curves after you transfer the data from D.1 and D.2 to your PC. Calculate the adsorbent capacity using Equation 1.

Note: based on the trial experiments, the mentioned rotameter setting would result in concentrations less than 490 ppm; so, steps # 11 and 12 are optional. Keep in mind that, in case the influent concentration gets close to 500 ppm, you can always decrease that by adjusting R.3 while the test is in progress. But, if you have followed steps # 11 and 12, you would start the experiment while D.1 is showing X (X <= 50 ppm). To regenerate the initial part of the curve for D.1, the readings/time until it gets to 50 ppm, you can use the average readings shown in Table 2.
Appendix B

SEM Micrographs of Feb.2016 Nonwovens

SEM micrograph of Feb.2016 unloaded CAD-27 webs – cross section

SEM micrograph of Feb.2016 unloaded C@D-32 webs – cross section

SEM micrograph of Feb.2016 unloaded CBD-37 webs – cross section
SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 325 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 845 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 1187 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 1514 g m$^{-2}$) – cross section
SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 3088 g m⁻²) – cross section
SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 3357 g m$^{-2}$) – cross section
SEM micrograph of Feb.2016 hybrid CAD-27 webs (AC: 3887 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 385 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 947 g m$^{-2}$) – cross section
SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 1348 g m$^2$) – cross section

SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 1704 g m$^2$) – cross section

SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 1996 g m$^2$) – cross section

SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 2525 g m$^2$) – cross section
SEM micrograph of Feb.2016 hybrid C@D-32 webs (AC: 3043 g m$^{-2}$) – cross section

SEM micrograph of Feb.2016 hybrid CBD-37 webs (AC: 333 g m$^{-2}$) – cross section
SEM micrograph of Feb.2016 hybrid CBD-37 webs (AC: 923 g m⁻²) – cross section

SEM micrograph of Feb.2016 hybrid CBD-37 webs (AC: 1307 g m⁻²) – cross section
SEM micrograph of Feb.2016 hybrid CBD-37 webs (AC: 1603 g m\(^2\)) – cross section

SEM micrograph of Feb.2016 hybrid CBD-37 webs (AC: 2046 g m\(^2\)) – cross section