A new generation of fibrillated acrylic fiber for high-performance nonwovens and specialty composites

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The fibrillated fiber permits the mechanical interlocking of various particles and fibers, imparting good mechanical strength to the material.

Acrylic fibers have outstanding resistance to water, chemicals, heat, and ultraviolet light. These fibers, in staple or in slightly fibrillated form, have been used in a number of nonwoven products to provide unique properties.

A new form of acrylic fiber has now been developed for which high degrees of fibrillation can be obtained. When this wet-spun acrylic fiber is subjected to special mechanical refining, it forms fibrils along the main filament, similar to cellulosic, asbestos, and aramid pulp. The fiber and fibrils entangle and bond and can be used in conventional wet-laid papermaking processes. Alternatively, the fibrillated acrylic fiber can be dried and used to entrap dry resins and fillers, which permits high loadings of these materials into the nonwoven.

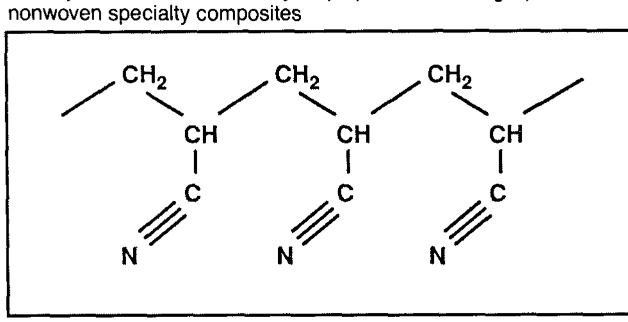
Here, we discuss the properties of acrylic fibers and fibrillated pulp. Various examples of new applications requiring high-performance nonwovens and specialty composites will show how the highly fibrillated pulp serves as a binder and as a means to improve product performance.

Polymer and pulp properties

This new acrylic fiber is composed of more than 90% polyacrylonitrile, with the structure shown in **Fig. 1** and a small amount of methyl methacrylate monomer to form a random copolymer. There is no surface finish or other additive. The surface charge is slightly anionic.

Generally, acrylic fiber spun for use in textiles does not fibrillate. DeLuca found that acrylic fibers produced for the textile markets do not disperse well in water, that they fracture rather than fibrillate during refining, and that resins added in some applications to impregnate the nonwoven do not provide an adequate bond (*1*). He correctly concluded that wet-spun fiber has an individual and unique structure that is not shared by the textile fibers.

1. Polymer structure of acrylic pulp used for high-performance nonwoven specialty composites



Wooding and Woodberry (*2*) have described products made from wet-spun acrylic fibers with modest degrees of fibrillation—that is, with a freeness above 450 mL CSF (Canadian Standard Freeness). However, fibers with this low a degree of fibrillation do not provide enough mechanical binding for a number of applications in nonwovens and specialty composites.

Recent work has led to the new type of fibrillated fiber. Starting with short wet-spun acrylic filaments, typically about 25 μm in diameter, a fibrillation process can be used to create a highly branched fibrillated pulp, as shown in **Figs. 2 and 3**.

Fibrils of various diameters are created, ranging from about a 10-μm trunk to fine branches of 1 μm or less. Control of the refining process permits the degree of fibrillation, measured in terms of the freeness, to be controlled from above 700 mL to less than 50 mL, while maintaining a nominal fiber length of greater than 5 mm. BET surface area can be as high as 45–50 m^2/g.

A summary of fiber and pulp physical properties is presented in **Table I**. In the refining process, branched structures are created to entrap and hold other components in the nonwoven. Long trunks remain to provide good web and finished sheet strength. For a fiber to have fibrils of such fine diameter is unique among synthetic fibers. The highly fibrillated acrylic has much greater binding and

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particle retention capacity in a nonwoven product than cellulose and aramid pulp.

This acrylic pulp also has higher thermal resistance than cotton-based or wood-based cellulose and many synthetic pulps such as polyester, polypropylene, and polyethylene. **Figure 4** shows a thermogravimetric profile of the new acrylic pulp over the temperature range of 20-600°C. Polyacrylonitrile fiber is used as a precursor for making high-performance carbon fibers. Because of the high polyacrylonitrile polymer content, the fiber is not thermoplastic and does not melt or smear on heating. Instead, it undergoes cyclization and carbonization when exposed to temperatures above 300°C.

The stabilization of restrained polyacrylonitrile fibers has been discussed extensively in the relevant literature (*3*, *4*). While the acrylic pulp does not melt, it can be thermally set to stabilize pleats or introduce dimples into the nonwoven. There is little difference in dry or wet sheet strength because the interfiber bonds are mechanically locked in during drying and are therefore relatively insensitive to moisture.

Processing

Depending on the particular application, this acrylic pulp can be produced either as a wet slurry (about 20% solids), a rolled wet-lap (about 50% solids), or as a dried fluff (greater than 96% solids).

Wet pulp disperses easily in water and can be used with various wet-lay paper machines to obtain specialty nonwovens or paper. Pulp has been successfully processed on cylinder, rotoformer, and fourdrinier paper machines. Normally, the pulp is dispersed in a hydropulper to break up any entangled fibers prior to the addition of other components. When using the highly fibrillated form of pulp with a freeness of about 60 mL CSF, as little as 5% binder fiber will interlock other fibers without the need for resinous binders. Commonly, 10–15% binder is used to provide good strength. With a pulp with a freeness of about 250 mL CSF, only about 40-50% acrylic pulp is required to entrap and hold particles while maintaining good paper strength.

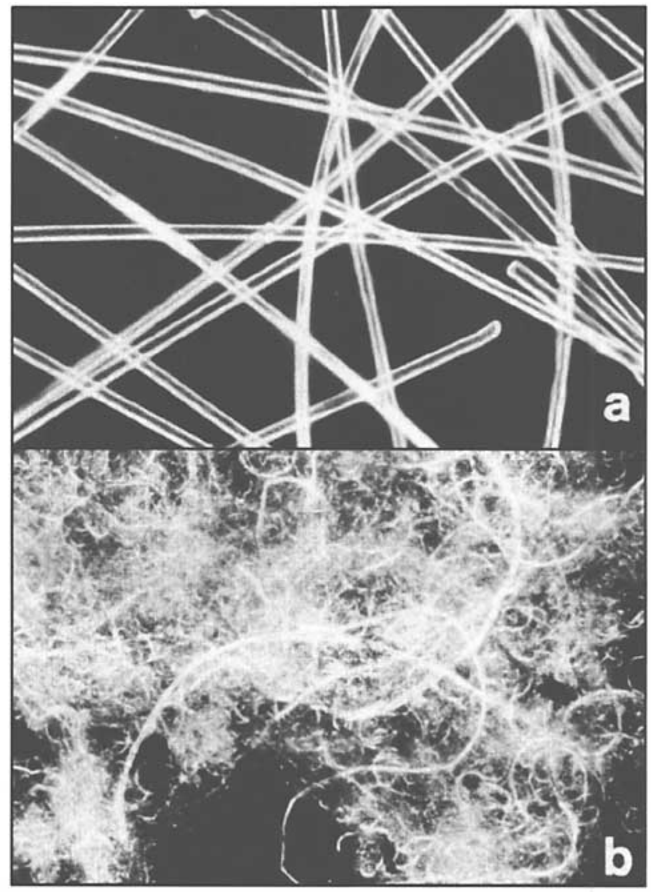
In dry mix compounds used in many specialty composites, plow or chopper mixers (such as the Littleford or Eirich mixers) are effective for opening and dispersing the dried fluff. Depending on the specific product, little pulp is required, perhaps to only minor percentages. When mixing the pulp with solvent-based resins, Sigma or Littleford type mixers have also been found suitable.

Products

Fibrillated acrylic fiber provides unique opportunities to engineer a variety of papers, nonwovens, and specialty composites, as **Fig. 5** illustrates. This new acrylic pulp is being used or evaluated in various types of high-performance applications based on several features:

- Ease of incorporation into paper stock
- Mechanical binding
- The range of fiber length and openness available
- Higher retention efficiencies with a synthetic fiber than achievable with alternative synthetic fibers
- Environmental resistance
- Temperature resistance and char yield
- More media stability in shocked or pulsed systems
- Improved homogeneity of media
- Increased performance in nonwovens
- Excellent fiber-to-resin adhesion in resin-impregnated papers

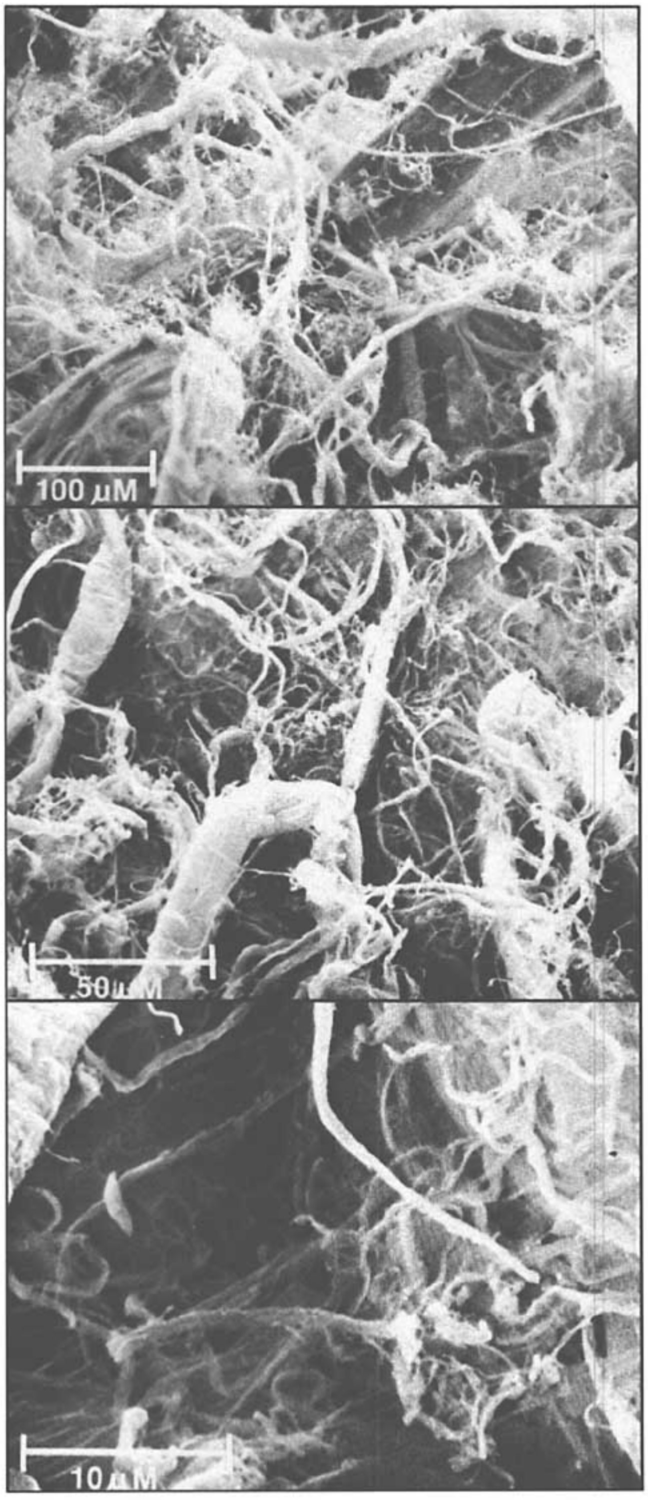
2. Photomicrographs (at same magnification) of (a) 25 μm staple and (b) wet pulp after fiber fibrillation



I. Physical properties of the new type of acrylic fiber

Density, g/cm³	1.17
Tensile strength, MPa	450
Modulus of elasticity, GPa	6.0
Elongation, %	15
Fiber length, mm	5-6.5
Freeness, mL CSF	35-700
BET surface area, m²/g	50
Moisture regain, %	<2.0
Surface charge	anionic

3. SEM photomicrographs of the branched structure, over a range of fibril diameters in acrylic pulp



To demonstrate the wide range of products possible using acrylic pulp, we will discuss examples that illustrate its use in specialty printing papers, combustible shell casings, filtration media, and as an asbestos substitute in friction materials.

Specialty printing paper

Acrylic staple can be processed in 100% form or in blends with cellulose pulp to form various grades and types of specialty paper or molded products. In earlier work, Bernier and Dobbins (*5*) showed that incorporating 5–25% of acrylic staple increases tear strength from 20% to 60% over that of 100% kraft paper, as shown in **Fig. 6**. The increase in tear strength can result in paper of lighter weight, which has many advantages including lower shipping costs.

Papers of 100% acrylic with a wide range of properties can be prepared by using the pulp, fibrillated to the desired degree, alone or in combination with acrylic staple. **Figure 7** shows a typical acrylic paper construction. Because of the high particle retention obtainable with this pulp, brighteners or other additives can also be easily incorporated. The use of 100% acrylic paper has the advantages of exceptional wet strength, moisture resistance, low shrinkage, resistance to sunlight (ultraviolet), and excellent chemical resistance. Acrylic paper can be easily dyed or printed over a wide range of dye shades with excellent light fastness. Products include outdoor signs, maps, and paper that requires chemical resistance. Acrylic pulp can also be used in blends with other pulp or identifier particles to create unique paper used in official documents, currency, stocks, bonds, and passports.

Combustible shell casings

One of the unique purposes of acrylic pulp is in combustible shell casings. As described by DeLuca (*1*), combustible cartridge cases are used in ammunition for tank guns and self-propelled howitzers. They are ordinarily composed of nitrocellulose, cellulose, and synthetic fibers molded to close tolerances to fit the gun firing chamber. They function to contain the main propellant charge and to contribute to its action. The cases disappear on firing and leave no smoldering residue. The use of the combustible cases saves metal, eliminates the disposal of spent cases, reduces weight, simplifies automatic firing equipment, and acts as a cleansing agent. Molded combustible cases are shown in **Fig. 8**.

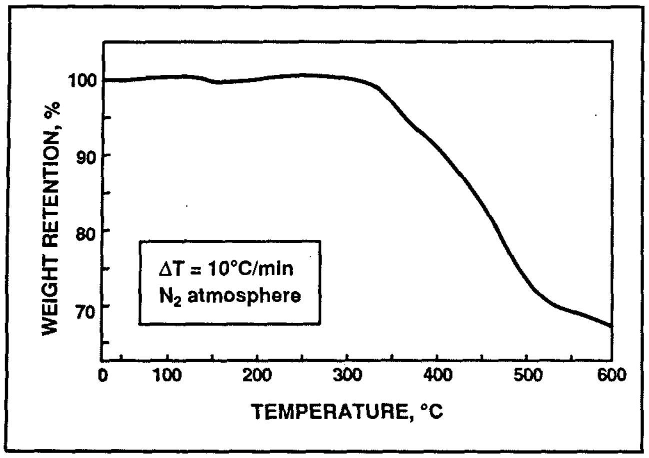
The assembled round may be stored for years. During storage, the cellulose fibers are exposed to the acid and oxidizing action of the oxides of nitrogen evolved by the propellant; consequently, they can be attacked and embrittled. Acrylic fiber will stand up to such attack indefinitely to provide reinforcement and strength when the round is handled.

Pulp molding methods are used in manufacturing shell cases. The fibers are slurried, specially refined to a relatively low degree of fibrillation of about 600 mL CSF, and beater-treated with resins. The stock is pumped at the desired consistency to felting tanks, and the preform is accreted by vacuum onto a screened form. The preform is dried under pressure in a heated, drained die. The part is then impregnated with a urethane varnish and cured, followed by punching, trimming, and gluing to fitting parts. Methods of manufacture have been discussed by DeLuca (*6*) and Williams (*7*).

Filter media

Greater concerns for the environment and increased awareness of health hazards are leading to fundamental

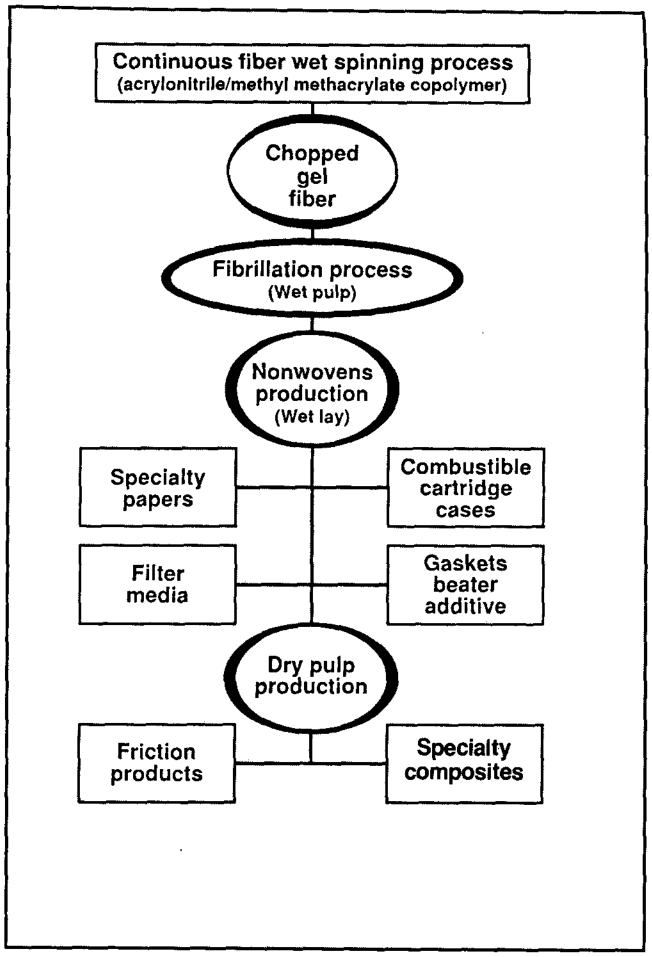
4. Thermogravimetric analysis profile of acrylic pulp



II. Physical properties of nonwovens containing binder and carbon powder

	Powder retention, %	*Tensile strength, kN/m*	
		Dry	*Wet*
Acrylic pulp	92.2	2.6	1.5
Acrylic pulp and cellulose pulp	74.2	1.8	0.5
Cellulose pulp	55.3	1.4	0.2
Cellulose pulp and acrylic staple	35.7	0.9	0.1
Acrylic staple	17.0	0	0

5. Process and applications diagram for acrylic pulp



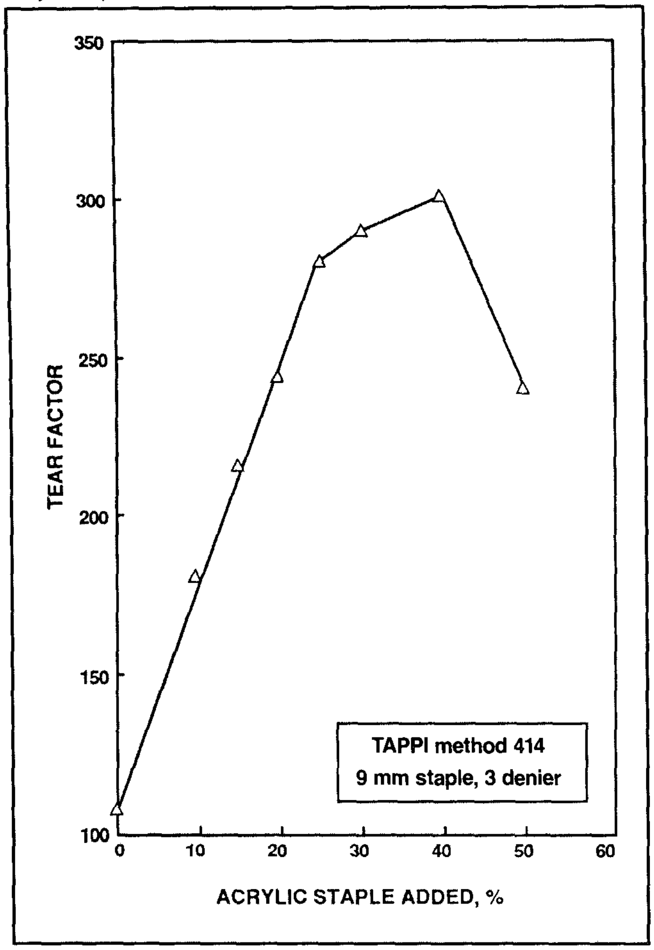
changes in both the commercial air and water filtration markets. Requirements are increasing for sorptive fillers based on activated carbon and for improved particulate filters based on fibers of high surface area. Granular and powdered active carbons have long been used to filter toxic vapors from air and water streams by adsorption. Recently, activated carbon fibers, with high dynamic adsorption characteristics, have also become available. One low-cost method of constructing thin sheets and felts from these fibers is the wet papermaking process. Since active carbon powders and fibers cannot be made self-bonding, a special binder must be added to give the sheet strength while retaining the active carbon. Commonly used adhesive binders are not recommended because these materials tend to block carbon micropores and diminish the adsorption characteristics.

New compositions of such materials can be made using fibrillated acrylic fiber as a binding agent for nonwoven, sorptive sheeting. Various combinations of activated carbon powder, activated carbon fiber, glass fiber, or other sorptive or mechanical obstruction components can be produced to meet air and liquid filtration needs over a wide range of applications. By organic adsorption, these filters can remove nuisance odors, toxic vapors, and lethal gases. Mechanically, such filters can obstruct particulates and aerosols.

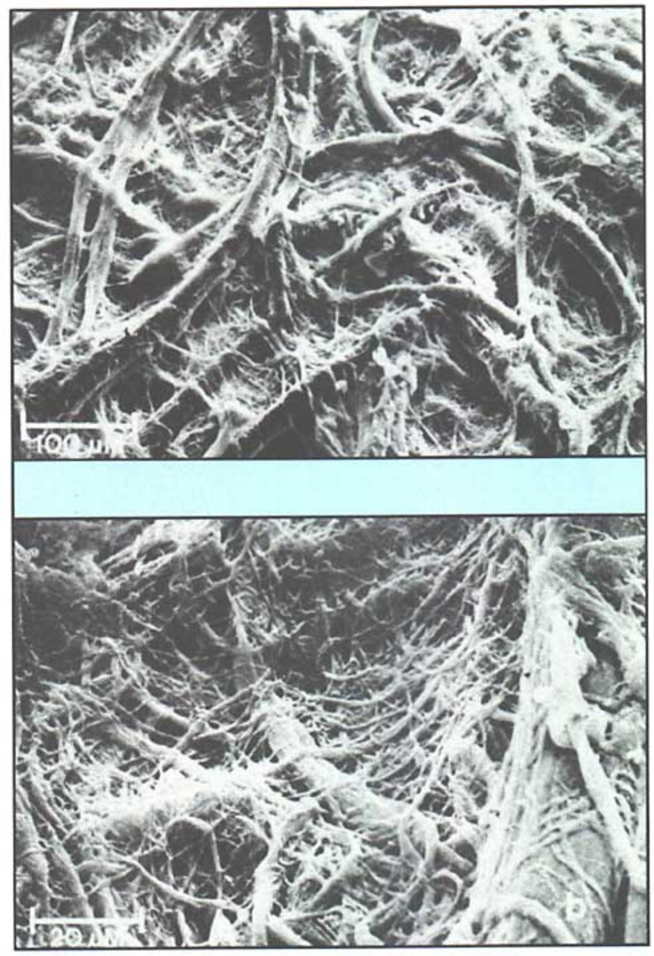
As described by Giglia (*8-10*), several novel nonwoven adsorptive felt-like structures having high loadings (by weight percent) of activated carbon fibers and/or activated carbon powders are possible by utilizing acrylic pulp as a binder. The use of this binder fiber permits extremely high loadings of filler materials such as activated carbon powders and fibers. The acrylic also helps to maintain good wet strength and chemical resistance. In **Table II**, the binder capacity and strength properties of acrylic pulp are compared with those of cellulose in a nonwoven containing equal weights of binder and fine carbon powder. These adsorptive papers with acrylic pulp binder exhibit organic vapor adsorption characteristics equal to the starting carbons. Also, the fibrillated fiber serves as a particulate filter through mechanical obstruction.

Active carbon paper bonded with fibrillated acrylic fiber has been made on various pilot and production paper machines. Formulations contain active carbon in the fine powder form, in fiber form, and as mixtures of carbon and other fibers. The acrylic pulp, active carbon, and processing additives were mixed by blending in a hydropulper before batches were added to the paper machine headbox for sheet forming. In all cases, the wet papermaking process using acrylic fiber produced a variety of highly adsorptive activated carbon mats, examples of which are shown in **Fig. 9**.

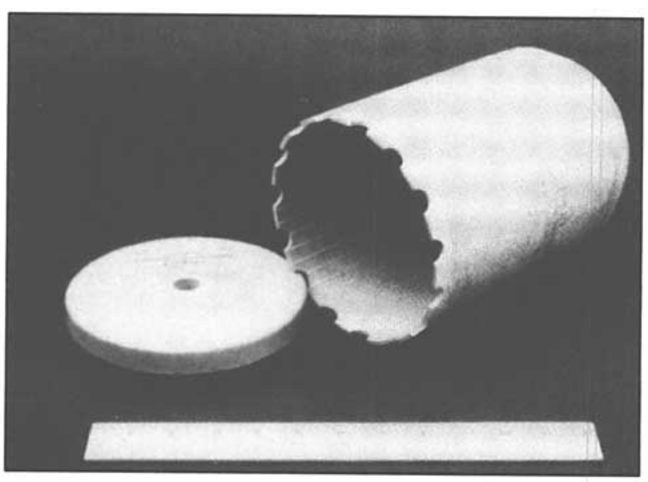
6. The tear strength of printing paper increases with the addition of acrylic staple.



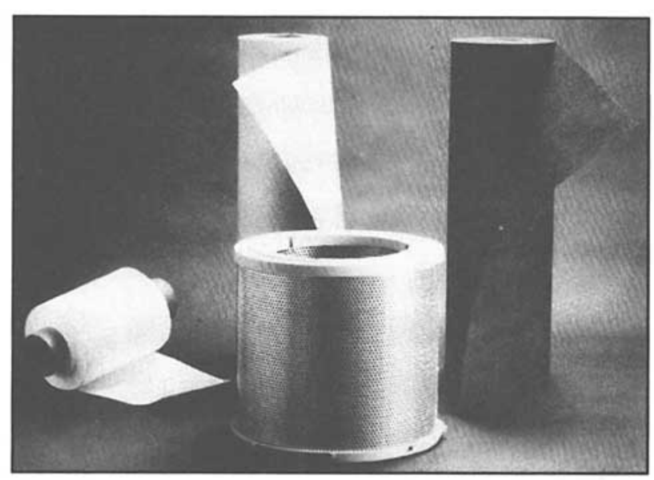
7. SEM photomicrograph of 100% acrylic pulp paper (250 mL CSF)



8. Pulp molded combustible shell casing represents a unique use of acrylic pulp in a long-term harsh environment.



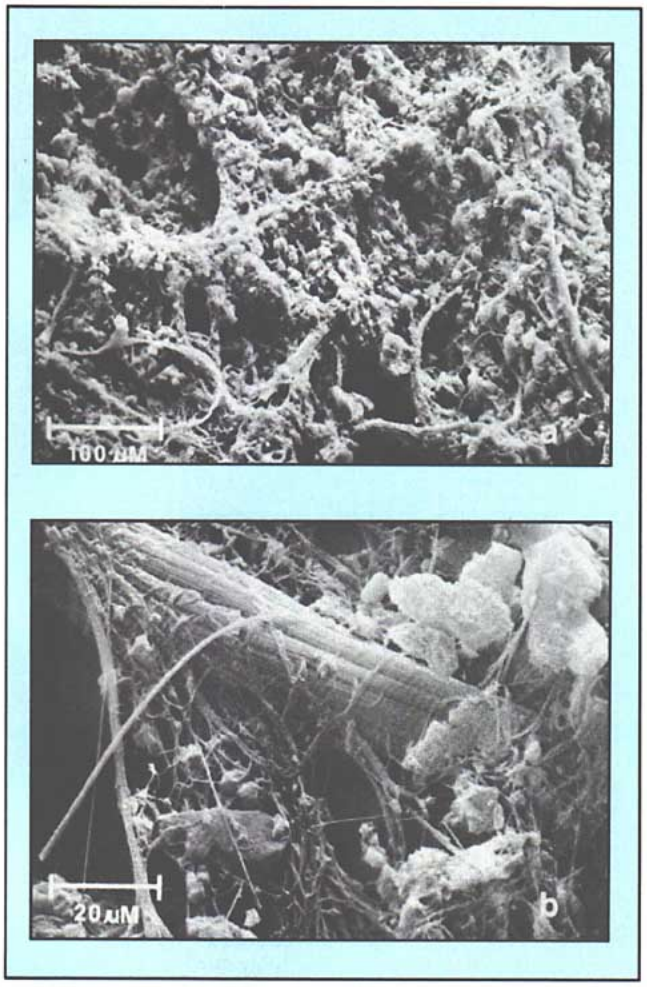
9. Adsorptive and aerosol nonwoven filter media and typical high-performance filter element



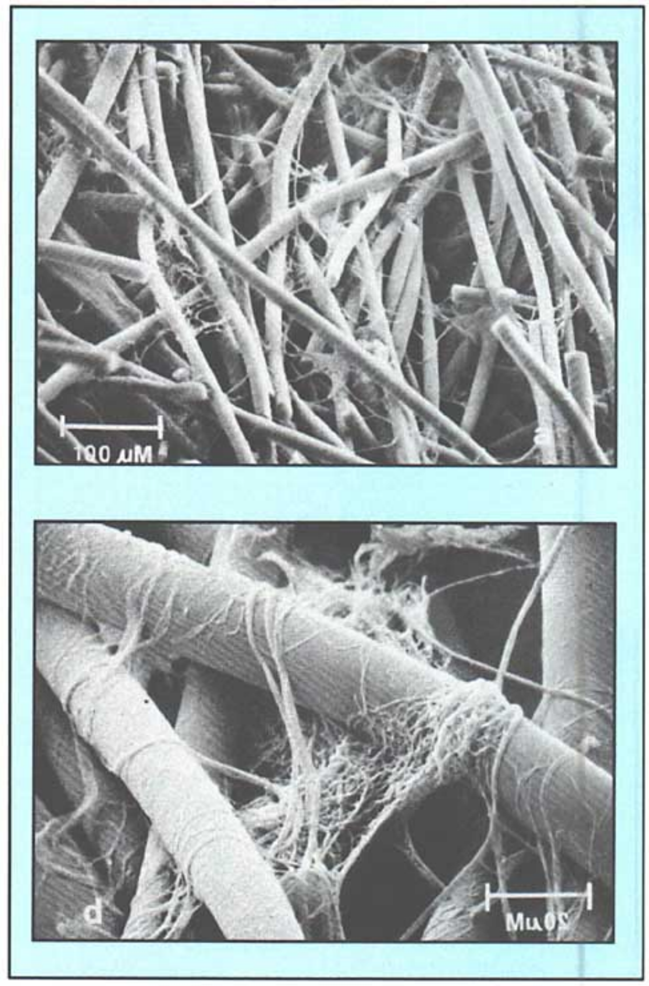
To use a nonwoven is to use a material that is easy to handle and process. The media can be rolled, pleated, or cut to the geometry desired. Mechanical binding eliminates resins and reduces filter break-away and brush off. Any type or form of activated carbon on other adsorptive material can be incorporated. The SEM micrographs in Figs. 10-12 illustrate the structures of various nonwoven media made with fibrillated fiber and activated carbons.

By using activated carbon fiber, increased flow-through rates, reduced pressure drops, and higher adsorptivity can be obtained. The high adsorption capacity and high adsorption rate of the fibers arise from the large

10. Water filter media with 45% acrylic pulp (250 mL CSF) and 55% activated carbon powder



11. Air filter media with 15% acrylic pulp (60 mL CSF) and 85% activated carbon fiber



concentration of the micropores directly on the surface. Manufacturers of these fibers have quoted adsorption rate values as much as 100 times greater than those observed on granular activated carbons. The superior dynamic adsorption characteristics of activated carbon fibers offer the opportunity to make filter structures that are thinner and lighter than those made using granular or powdered active carbons.

A reduction in the critical bed depth allows for smaller filtering systems, which holds down operating and investment costs. For example, because of the low flow resistance and high adsorbence of carbon fibers and acrylic pulp media, compact filter systems with low power input have been specified for portable recirculation units required for military purposes. No other commercial or developmental media were found that met the specifications.

The fibrillated acrylic is also attractive for use in aerosol and HEPA (high-efficiency particulate-arresting) filters for which microglass is normally used. As shown in Figs. 3 and 12, the fibril of the acrylic may be near micron size or submicron size. By incorporating acrylic pulp into microglass filters, shredding can be reduced, and strength can be improved. For aerosol entrapment, it is possible to make 100% fibrillated acrylic sheets that have high dioctylphthalate resistance while maintaining acceptable air flow.

Applications of acrylic pulp in filtration include: portable water cartridges, industrial fluid cartridges, HEPA filters, military face mask media, and specialized absorbent filter media.

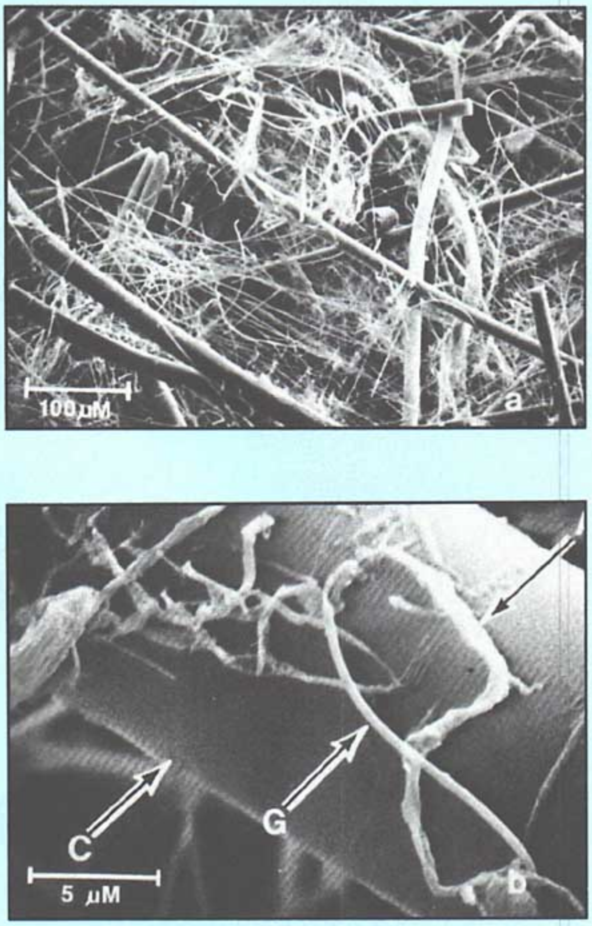
Asbestos substitution

Certain health hazards that stem from exposure to asbestos have been recognized for many years. A recent Environmental Protection Agency Final Rule prohibits, at staged intervals, the future manufacture, importation, processing, and distribution in commerce of asbestos in almost all products (*11*).

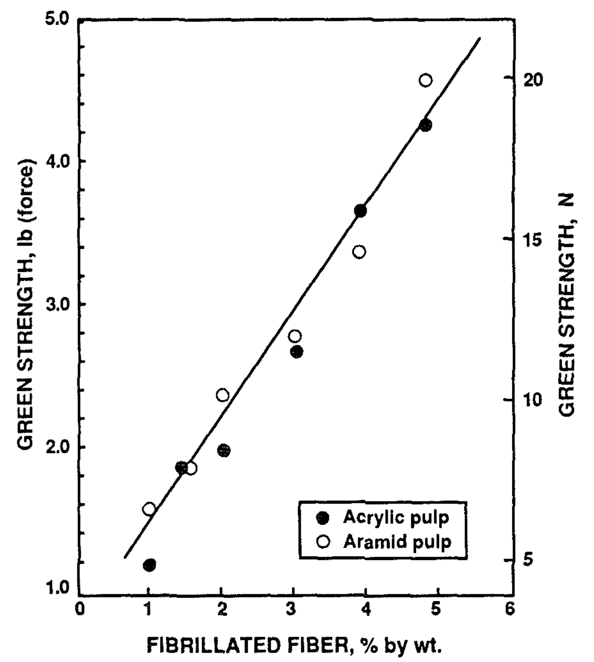
Asbestos has been a major ingredient of many compositions for the past century, including friction materials, gaskets, roofing and flooring materials, coatings, and sealants. It was widely used because of its highly desirable functional properties and processing versatility and because it was economically attractive.

In the production of composite materials such as brake and clutch friction materials, asbestos is used to reinforce the composition. The reinforcing fibers not only impart desirable characteristics to the final product, they also provide "green strength" during preforming of the composite, when the composition mixture is compacted at

12. Adsorptive and aerosol filter media with 10% acrylic pulp (60 mL CSF), 50% activated carbon fiber, and 40% microglass



13. Acrylic pulp is used to provide green strength in nonasbestos friction materials.



ambient temperature prior to final hot molding. The "green strength" function of the asbestos resides in the fact that fiber bundles can easily be "opened" to provide a fiber mass that displays a large surface area per unit weight. This large surface area leads to strong binding of frictional compositions.

Many substitute materials have been tried in friction products, but few have proven fully satisfactory in commercial practice. Two principal reasons for the lack of success have been inadequate preformability and high costs.

If the degree of fibrillation and fiber strength of the acrylic fiber are controlled, this pulp serves as an effective processing aid to provide the needed green strength in dry-processed automotive disc pads and truck blocks (*12*). For a typical nonasbestos automotive disc pad formulation, **Fig. 13** compares the green strength for acrylic and aramid pulps currently used in many friction materials. **Figure 14** shows typical molded nonasbestos brakes that were processed using acrylic pulp to provide green strength after initial cold pressing.

Transmission papers are examples of wet-laid nonwovens products in which acrylic pulp is used in place of asbestos. Energy absorption and transmission devices that operate in oil require unique friction materials that are distinct from dry-molded brake products such as disc pads, linings, and truck blocks. Wet friction materials are used in automatic transmission plates and in a number of transmission, clutch, and wet brake devices in off-highway vehicles and industrial equipment.

Porous felt, up to 4 mm in thickness, is produced using a wet-laid process on a paper machine. The base paper formulations may include cellulose, aramid, other fibers, and fillers such as diatomaceous earth, graphite, abrasives, and in some cases latex or phenolic resin. The paper is either blanked into rings, saturated in phenolic resin and cured, or saturated in sheet form and then blanked. Rings with cured resin are bonded to steel cores and machined. Machining can include rather complex groove patterns to control oil flow. The sustained temperature that a friction material can withstand is determined by the binders and other materials which form its continuous matrix. Therefore, thermal stability in the range of 400°F is critical in the selection of new organic paper materials. Acrylic pulp is being evaluated in this application both as a means to improve the performance of cellulose-based materials and to reduce the cost of aramid-based materials.

The development of nonasbestos packing and gasket materials has also been a highly active area in recent years. New materials and constructions are constantly being developed to meet industry needs. Matzka (*13*) has reviewed several types of fibers, including acrylics, which are predominantly used today.

Gaskets reinforced with nonasbestos fiber are either formed by a beater additive or a calender process. In the beater additive process, fibrous and particulate fillers are beaten together with a cement, rubber latex, or starch binder in a water slurry and made into gasketing on a paper machine. In this process, the fibers must be opened and distributed sufficiently to form a web capable of carrying the particulate fillers and the binder. It must also be possible to create an attraction between the fibers and the binder so that they coalesce to form a cohesive structure as the water is drained away. The new acrylic pulp meets these processing requirements. Depending on the particular gasket product, the acrylic pulp has been used alone or in combination with either cellulose, aramid, or glass to provide more technical alternatives to engineer nonasbestos gaskets.

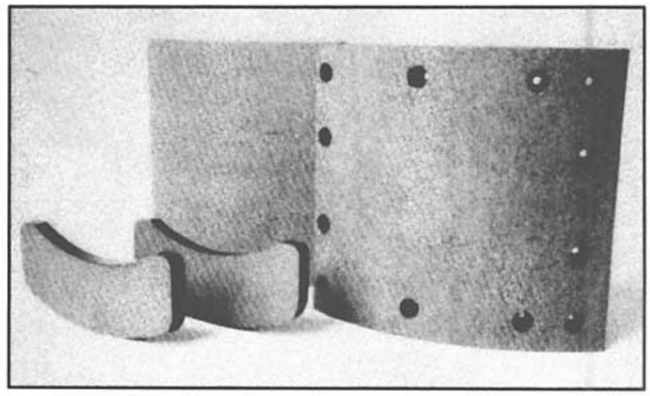
Summary

The advantages of acrylic fiber in nonwovens have long been recognized. The industry has used both staple and slightly fibrillated fiber in a number of products. However, full utilization of acrylics was not possible in the past because it has not been possible to fibrillate material to a sufficiently high degree on a commercial scale.

Highly fibrillated, high-surface-area acrylic pulp has recently been developed for use in specialty materials and high-performance nonwoven products. This pulp has fibrils that are near 1 μm in size, which is unique for a synthetic pulp. In addition, the temperature resistance of the acrylic pulp is higher than other synthetic pulps commonly used in nonwovens production. The pulp can be produced in both wet and dry forms, with the wet lap providing excellent dispersion in aqueous systems. The fibrillar structure and long fiber length enables the acrylic pulp to act as a mechanical binder to provide strength and to entrap small particles.

The fibrillated fiber can be used to modify or enhance the performance properties of a paper or nonwoven product based on its physical characteristics and environmental resistance. The acrylic pulp has been used for high-performance adsorptive and particulate filtration media and as a substitute for asbestos and aramid in friction materials and gaskets. It has also been used in combustible shell casings and in specialty papers ranging from speaker cones to pavement markers to official document papers. In addition, because the range of fibrillation and fiber length can be controlled in the fibrillation process, acrylic pulp properties can be engineered and controlled to meet many other specialized requirements.□

14. Nonasbestos automotive disk pad and truck block containing acrylic pulp



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