

# Novel Microporous Films and Their Composites

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## ABSTRACT

Cost-effective microporous films and composites can be made by using polyolefinic material and inorganic fillers. These microporous films and their composites can be designed and manufactured at high speed using commercial equipment for disposable hygiene articles, protective health care garments, building construction and many other industrial applications where air and moisture breathability is needed. The theory, formulations and methods of making these cost-effective polyolefinic-calcium carbonate compositions are discussed. Special engineering fibers and their fabrics can be combined with these novel microporous films to achieve a variety of properties for practical applications. However, one should keep intellectual property considerations in mind when contemplating the manufacture of microporous film products, their companies and their applications.

## INTRODUCTION

Breathability in polymer films and film composites generally relates to the ability of the film or composite to allow the passage of moisture vapor. Breathability of a material is usually measured by its moisture vapor transmission rate (MVTR), also known as water vapor transmission rate (WVTR). Early examples of breathable polymer films and composites date to 1976 with the introduction of GORE-TEX®<sup>(1)</sup> (a two or three layer composite of fabric and microporous polytetrafluoroethylene [PTFE] film, used for outerwear such as shoes, gloves and jackets) and BION II<sup>(2)</sup> in early 1980 (a fabric with a monolithic polymer coating, providing absolute waterproofness yet a high degree of comfort through its moisture vapor permeability, used for wound dressings and fabrics). Since that time, research to develop cost-effective breathable polymeric films and microporous film composites using nonwoven, woven or other fabrics, which are then used for disposable and limited use articles, has bloomed.

Nonporous, solid polymer membranes made of polymer resins that allow the passage of water vapor because of the hydrophilic character of the resin itself

are known as monolithic membranes or films. Polymers such as thermoplastic polyurethanes, DuPont's Hytrel® and DSM's Arnitel® (both polyether block ester elastomers), and Atochem's Pebax® (a polyether block amide elastomer) are resins that can be fabricated into monolithic films. Gore-Tex® film is expanded microporous PTFE, which is an expensive polymeric material. All these raw materials are extremely expensive when compared to well-known and widely used polyolefins such as polyethylene and polypropylene and their copolymers.

One objective of this paper is to discuss alternative techniques for making cost-effective microporous films using conventional polyolefinic materials with inorganic fillers. Another objective is to demonstrate combinations of these cost effective microporous films with nonwoven, woven and other special fibers and fabrics to make cost effective disposable and limited-use articles. Typical applications include products in the hygiene, medical, protective garment and building and construction markets.

## MICROPOROUS FILMS

One general characteristic of a water barrier microporous breathable film is that the film contains billions of micropores, and many of these micropores are connected (see *Figure 1*, which illustrates a typical microporous polymer-calcium carbonate [CaCO<sub>3</sub>] structure). The pore sizes are smaller than a drop of water, so water droplets such as rain can not penetrate unless extraordinary pressure is applied. However, the pores are much larger than water vapor molecules, so steam and perspiration can readily penetrate the film and pass from one side of the film to the other. More specifically, these types of films can also be used for applications such as filtration and protective garments. In these applications, it may be important to know the pore size and size distribution of the particles one wants to filter or block, in order to guard against the penetration of the particles through the micropores. *Figure 2*<sup>(3)</sup> presents the sizes of various particles and a relative comparison among those particles, including water droplets, water vapor, HIV virus, human hairs, etc.

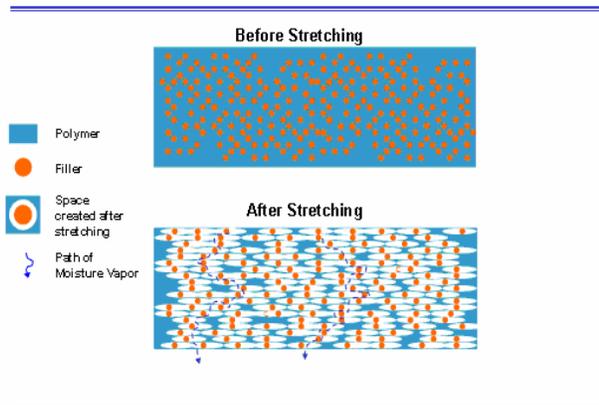


FIGURE 1. Moisture vapor migration through microporous film

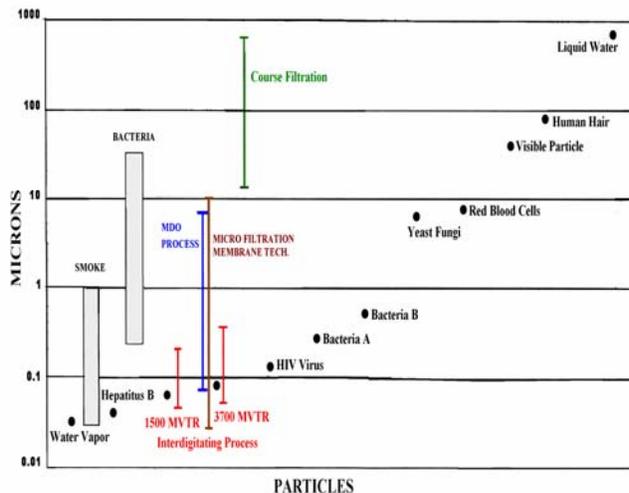


FIGURE 2. Comparison of various particle sizes

(This chart is for a general purpose use only. One must verify the precise size of the particles of concern for any real product application.)

### Formation of Micropores in Plastic Films

If the stress level is high enough and the rate of deformation is fast enough, most unfilled plastic films will undergo stress cracking and form micropores. Under these conditions the film will appear opaque due to light scattering from the small pores that are generated. This phenomenon has been described in great detail in Barenblatt's theory on the mechanics of deformation, flow, and fracture of polymers in the early 1970's<sup>(4)</sup>. Unfortunately, under normal ambient conditions of our surrounding environment, most unfilled plastic materials will not stress crack and become microporous. Even if some

stress cracking occurs, the number of pores is not high enough to allow pore-to-pore connections that form the tortuous paths necessary for air and moisture to flow through easily.

Fortunately, the 1966 publication of Great Britain Pat. Nos. 1,044,028, entitled "Improvements Relating to Filled Polyolefine (*sic*),"<sup>(19)</sup> and 1,044,502, entitled "Stretched Polyolefin Compositions,"<sup>(20)</sup> to W.R. Grace & Co., demonstrated that mixtures of polyolefins and inorganic fillers can be stretched under normal ambient conditions and easily achieve the necessary stress level (force) and strain rate (rate of deformation) needed to form microporous films.

In 1976, Schwarz<sup>(24)</sup> described the formation of synthetic paper by stretching polymer films comprising blends of dissimilar and incompatible polymers. Cited examples of such polymer blends included blends of polypropylene and polystyrene and blends of polyethylene and nylon 6-6. In these blends, the semi-crystalline polyolefin serves as the matrix of the film. The incompatible polymer is either an amorphous polymer or a crystalline polymer with a glass transition temperature at least about 40°C higher than the matrix polymer. The incompatible polymer is not homogeneously dispersed through the matrix polymer, but rather is distributed as a submicron to micron-sized emulsion within the matrix. The dispersed polymer phase may also consist of rigid inorganic filler such as calcium carbonate, clay, or titanium dioxide. It is believed that the adhesion between the matrix polymer and the dispersed phase is poor, and microvoids will form around the dispersed phase inclusions when the composite film is stretched.

The development of suitable technologies involving stretching techniques and material formulations combining polyolefins and inorganic fillers to form air and moisture vapor breathable films has resulted in many practical applications, including disposable baby diapers and medical drapes and gowns.

### Polyolefin-Calcium Carbonate Microporous Films

The article published by Cancio, Jezzi and Wu entitled "The Evolution of Microporous Film," in 2004<sup>(5)</sup> described microporous film materials in great detail. Various compositions have been described for use in making microporous films. In the early years (1960's-1980's), it was thought that microporous film formulations needed to contain processing additives such as paraffin oil<sup>(19, 20)</sup> or glycerine monostearate<sup>(25)</sup> in addition to the polymer and filler. However, these additives were expensive and/or they were difficult to process, causing problems such as

excessive smoking during film extrusion. Later, it was found that cost-effective compositions containing only polyolefins and inorganic filler could be used. These polyolefins are typically polyethylene, polypropylene, and their copolymers. Polyethylene polymers include LDPE, HDPE, LLDPE and metallocene PE. The polypropylene can be conventionally catalyzed PP or metallocene PP. The inorganic filler can be calcium carbonate (CaCO<sub>3</sub>), barium sulfate, or other finely powdered inorganic materials. The polyolefin/filler blend is extruded as a “precursor” non-porous film, and then the precursor film is stretched mechanically to form a microporous film that provides air and moisture vapor breathability.

As mentioned in Section II-A, unfilled polymer films cannot be readily stretched to form microporous films by stress cracking under ambient conditions. However, filled polymer films or materials comprising polyolefins and fillers such as calcium carbonate may be easily stretched at room temperature or at elevated temperatures to form microporous materials. It has been found that the moisture vapor transmission rate (MVTR) of such filled polymer microporous films will increase when the film is stretched at elevated temperatures, as long as the stretching occurs at a temperature below the melting point of the polymer matrix.<sup>(28)</sup> Additionally, the morphology of the matrix polymer plays a significant role in the formation of micropores. Both heat and the polymer’s degree of crystallization will enhance the cavitation process by which micropores are formed.

When one talks about MVTR results or values for microporous materials, one must also refer to the test method that was used in order to understand these results. This is because the test method and test conditions can dramatically affect the results of the MVTR measurement. *Table I*<sup>(6)</sup> demonstrates the MVTR values measured for typical polyethylene/calcium carbonate microporous films by three different testing methods. In each column, the same film is measured by all three methods. As one can see, the choice of test method gave dramatically different test results for the same film; in each case, the result measured by ASTM E96(B) is roughly 10X less than the result for the same film measured by ASTM F1249.

The transport of water through a barrier material will, of course, depend on the difference in the water vapor pressure on either side of the barrier. In turn, the water vapor pressure on each side of the barrier will depend on the temperature and relative humidity

conditions. Water vapor will transport from the side with higher water vapor pressure to the side with lower vapor pressure. For monolithic breathable films, MVTR also depends on the thickness of the film. For microporous breathable films, MVTR depends on the pore sizes, the pore size distribution, and the number of tortuous paths of interconnecting micropores through the thickness of the film (see *Figure 1*).

Table I  
Effect of Test Method on MVTR Measurement  
(PE/CaCO<sub>3</sub> Microporous Film)

Test Method	Measured MVTR (g/m <sup>2</sup> /24 hr)			
	Film I	Film II	Film III	Film IV
ASTM F1249 <sup>(1)</sup>	4,500	5,500	8,000	10,000
ASTM E96(E) <sup>(2)</sup>	2,000	2,200	2,500	3,200
ASTM E96(B) <sup>(3)</sup>	650	720	800	920

(1) MVTR measured using a modulated infrared sensor. Test conducted at 37.8°C (100°F). Also called “MOCON MVTR (or WVTR) test.”

(2) MVTR measured using dessicant in a vessel sealed with the test film. Vessel is weighed to determine MVTR. Test conducted at 37.8°C (100°F).

(3) MVTR measured using a water-filled vessel sealed with the test film. Vessel is weighed to determine MVTR. Test conducted at 23°C (73.4°F).

For all of these reasons, the measurement of MVTR can be confusing or meaningless unless one knows the method and conditions by which MVTR is measured. Additionally, one should select the appropriate MVTR test method that reflects the conditions under which the breathable film will be used in the final product. Certainly, the measurement of MVTR can be tedious and time-consuming. The method of choice for quickly determining MVTR is ASTM F-1249, which uses test equipment from MOCON. It is important to accurately calibrate the measuring equipment in order to achieve accurate and reproducible results.

One factor that can affect the size of the micropores, and hence the MVTR and breathability, of a microporous film or composite is the particle size and particle size distribution of the filler (e.g. CaCO<sub>3</sub>) in the microporous material. In *Figure 3*,<sup>(6)</sup> examples of different average particle sizes and the measured air flow through various microporous films are given. It is reasonable to assume that at the same weight percent loading of CaCO<sub>3</sub> and at the same degree of

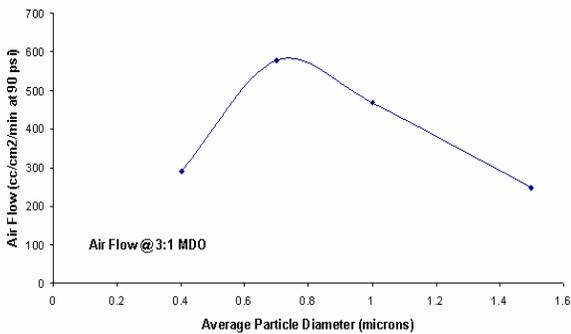


FIGURE 3. Effect of mean particle size on breathability

stretching, the much smaller particles (in this case, 0.4 microns) are less easily cavitated, but can form many and much smaller pores. When the average particle size is bigger (in this case, 1.5 microns), it can cavitate to form bigger pores, but there are fewer particles in the 1.5 micron system than in the 0.4 micron system at the same weight percentage. Accordingly, the pore sizes and number of pores are competing factors in formulations that contain an equal weight percentage of CaCO<sub>3</sub> loading. So, it is not unreasonable to assume there is an optimized particle size and distribution to get the maximum breathability. *Figure 4* demonstrates the surface topology of the formulations shown in *Figure 3*. U.S. Pat. Pub. 2004/0157333 (McAmish et al.)<sup>(26)</sup>, assigned to Clopay Plastic Products Company, Inc., describes the micropore structure of a microporous film as determined using three-dimensional imaging technology.

Typically, a microporous film composition contains about 50 ± 10% by weight of inorganic filler, with the balance being one or more polyolefin polymers such as polyethylene and/or polypropylene. To ensure the pores connect together through the film thickness, there must be enough inorganic filler present, and the film must be stretched enough to form micropores that can interconnect to form pathways through the film. *Figure 5* shows the influence of the calcium carbonate loading on the MVTR of a PE film<sup>(6)</sup>.

We have found that filled polypropylene films form smaller micropores than do filled polyethylene films at the same filler loading and degree of stretching. We believe this is due in part to the morphological differences, such as crystalline forms, between the two polymers, and also because adhesion between the matrix polymer and the rigid calcium carbonate filler is different. We believe polypropylene has better ad-

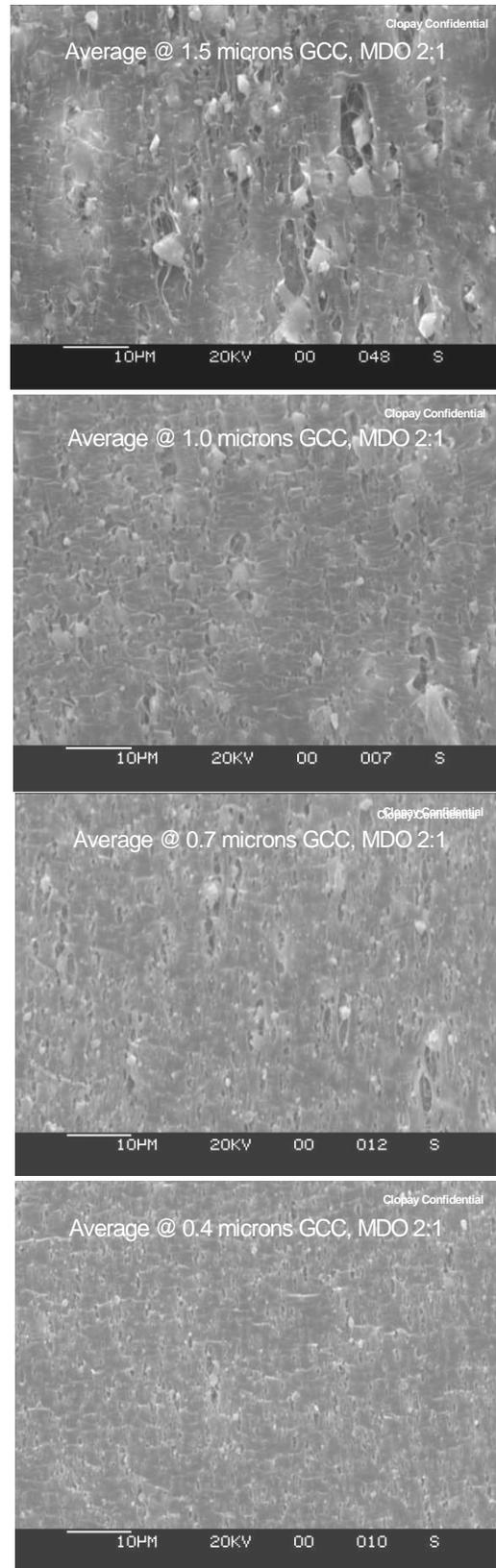


FIGURE 4. The effect of mean particle size on surface topology

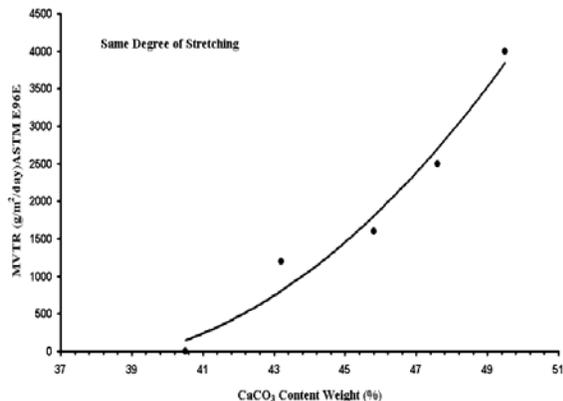


FIGURE 5. Correlation of MVTR and calcium carbonate content

hesion to the filler than does polyethylene. As stated earlier, in the formation of microporous films, the microvoids will form around the dispersed phase inclusions upon stretching. We have also found that the mean pore size of multilayer films of PE and PP will also vary with the layer arrangement (i.e. ABA vs. BAB). A direct comparison of mean pore size when using PE and PP in multilayer microporous films is shown in Figure 6, as demonstrated in U.S. Pat. Pub. 2003/0035943 (Jones et al.)<sup>(7)</sup>, assigned to Clopay Plastic Products Company, Inc. Adjusting the polymer matrix and the layer arrangement of multilayer films allows one to make novel microporous films with controlled properties such as pore size, pore size distribution, air and moisture permeation rate, and leakage barrier. This novel means of controlling the properties of a microporous material has practical importance in industrial applications.

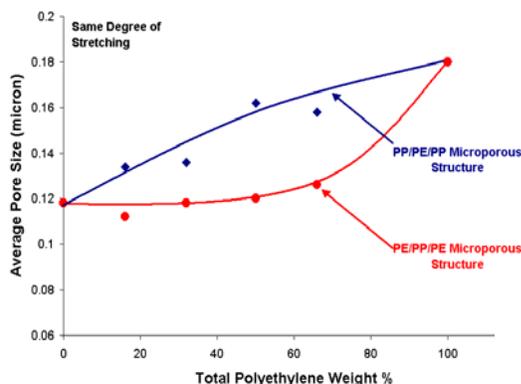


FIGURE 6. Influence of polyethylene on average pore size

## Stretching Techniques For Making Microporous Films

There are three common techniques for stretching microporous film precursor to render the film microporous<sup>(5)</sup>.

One common process, called machine direction orientation (MDO), involves passing the film between at least two pairs of rollers. Figure 7 demonstrates this process. The second pair of rollers ( $T_2$ ) is running faster ( $V_2$ ) than the first pair of rollers ( $T_1$  and  $V_1$ ). The ratio of  $V_2/V_1$  determines the degree of stretching. A second common technique is called cross machine direction tentering, as shown in Figure 8. This entails grabbing the side edges of the web and stretching the web sideways. For many years, this was the only way to stretch the film in the cross machine direction. The process is slow and because the forces are concentrated on the edges of the film, it often does not stretch the film evenly.

The third film stretching technique is called incremental stretching, intermeshing or interdigitating stretching. This is the method described in US Pat. Nos. 4,153,751 (Schwarz)<sup>(21)</sup>,

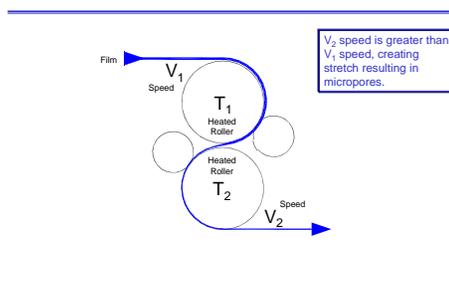


FIGURE 7. Machine direction orientation (MDO)

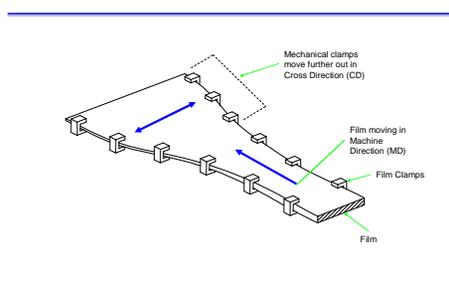


FIGURE 8. CD stretching by tenter frame

4,153,664 (Sabee) <sup>(22)</sup>, 5,202,173 (Wu) <sup>(8)</sup> and 5,865,926 (Wu) <sup>(10)</sup>. The film passes between two grooved or toothed rollers as shown in *Figure 9*. The grooves or teeth intermesh without touching each other when the rollers are brought together. As the film passes between the two rollers, it is stretched as it zigzags between these intermeshing teeth. Stretching by intermeshing has the advantage of causing the film to stretch in many small increments that are evenly spaced over the entire film in the machine direction (MD), the cross direction (CD), at oblique angles to the MD, or in any combination of these. The depth to which the intermeshing teeth engage controls the degree of stretching.

Accordingly, by carefully choosing materials and manufacturing conditions, novel microporous films can be easily produced on an industrial scale with a controlled range of properties. These novel microporous materials are cost-effective both because

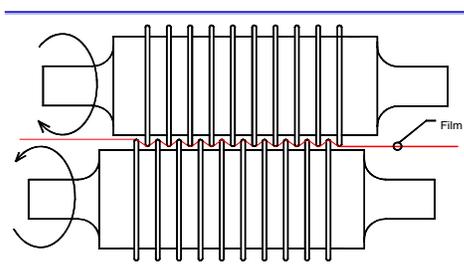


FIGURE 9. CD intermeshing rolls-closed

of the relatively inexpensive materials used and the high-speed methods of manufacture. One can use low cost raw materials, polyolefins and inorganic fillers, and incrementally stretch the precursor to make microporous film for many industrial applications. What polymeric materials are cheaper than PE and PP? Which inorganic filler can be cheaper than calcium carbonate (a rock)? The combination of these two materials with a very economical process should make microporous films the winner in the marketplace.

#### **Typical Microporous Film Properties**

As described in Section II-B above, any polyolefin material can be blended with about 50±10% calcium carbonate by weight, without expensive processing additives such as those described in the literature <sup>(19, 20, 23)</sup>. With this simple formulation in mind, many cost-effective films can be produced by the

incremental stretching process. *Table II* demonstrates typical properties of these microporous films. *Table III* gives a general comparison of intermeshed films and commercially available MDO films. At the same gauge and same MVTR level, we have found that MDO film has higher mean pore sizes as well as broader pore size distributions than CD and MD intermeshed films. Depending on the application, one can reasonably choose a microporous film produced either by MDO process or intermeshing process or combined processes as demonstrated in U.S. Pat. No. 6,811,643 (McAmish et al.) <sup>(18)</sup> and U.S. Pat. Pub. No. 2005/0248051 (Cancio et al.) <sup>(17)</sup>.

Further, microporous films with elastic properties can be made if the polymer matrix is elastomeric. For instance, films from very low density polyolefins that are synthesized by single-site catalysis can be elastomeric. Other thermoplastic elastomer polymers can be used instead. Blending elastomeric polymer resins with filler, forming a film, then mechanically stretching the film will produce an elastic microporous film that will stretch and recover. <sup>(27)</sup>

#### **MICROPOROUS COMPOSITES**

The novel microporous films described above can be combined with specialty fabrics to make microporous composites. Fabrics provide a cloth-like feel to these composites. Fabrics also enhance the mechanical strength of the composites, which is of practical importance in many applications. Composites of microporous films and fabrics enjoy the advantages of the liquid-barrier properties of the film and the strength and aesthetics of the fabric.

A microporous film can be bonded to a fabric through processes such as adhesive lamination, thermal bonding, ultrasonic bonding, etc. Better yet, the microporous formulation precursor film can be combined with fabrics such as nonwovens or wovens through extrusion coating or lamination. This extrusion-coated composite or laminate material can then be stretched simultaneously to form a microporous composite, as revealed in U.S. Pat. No. 5,865,926, <sup>(10)</sup> assigned to Clopay Plastic Products Company, Inc.

This technique produces an adhesive-free cloth-like microporous laminate of a nonwoven fibrous web and breathable plastic film, a laminate that combines air and moisture permeability with liquid barrier properties for disposable hygiene, health care, and protective apparel products.

*Table IV* demonstrates the properties of microporous composites using typical spunbond polypropylene

**Table II.** <sup>(1)</sup>  
**General Microporous Film Properties produced by the Intermeshing Stretching Process**

Grams weight of Film (g/m <sup>2</sup> )	10	20	30	40	
MVTR (ASTM E96E, g/m <sup>2</sup> /day) <sup>(2)</sup>	1000-4500	1000-4000	1000-4000	1000-4000	
MVTR (Mocon, 37.8 C, g/m <sup>2</sup> /day) <sup>(2)</sup>	3000-12,000	3000-10,000	3000-10,000	3000-10,000	
Air Flow (cc/cm <sup>2</sup> /min at 90 psi)	200-1600	200-1500	200-1500	200-1500	
Average pores sizes (Microns) <sup>(3)</sup>	0.07+/- 0.02	0.07+/-0.02	0.07+/-0.02	0.07+/-0.02	
Pore Size Distribution (microns) <sup>(3)</sup>	0.04-0.25	0.04-0.25	0.04-0.25	0.04-0.25	
Main Pore Range (80%+ of pores) (Microns)	0.05-0.10	0.05-0.10	0.05-0.10	0.05-0.10	
Max. Tensile Strength (N/cm)	MD	2.0-5.0	4.0-6.0	5.0-6.0	5.5-7.0
	CD	0.5-1.0	1.0-2.5	3.0-5.0	3.5-5.5
Elongation at break (%)	MD	100-300	200-350	250-400	250-400
	CD	100-400	300-550	350-600	350-600

1: Film formulations have been described qualitatively in the text; detailed formulations are Clopay proprietary information.

2: At any thickness, the MVTR and air flow depends on the degree of stretching.

3: Pore size and pore size distribution of PP is lower than PE.

**Table III.** <sup>(1)</sup>  
**A Comparison of Properties of Intermeshed Film and MDO Film**

Microporous Film Type	CD and MD Intermeshed Film	Commercial MDO Film	
Film Basis Weight (grams/m <sup>2</sup> )	25-40	25-40	
MVTR (ASTM E96E) (g/m <sup>2</sup> /day)	1000-3500	1000-3500	
Mean Pore Sizes (microns) <sup>(2)</sup>	0.07+/-0.02	0.23+/-0.04	
Largest Pore Sizes (Micron) <sup>(2)</sup>	0.25+/-0.05	1.2+/-0.5	
MD Tear Strength (grams) <sup>(2)</sup>	Notched	100-150	30-50
	Un-notched	500-600	300-400

1: Film formulations have been described qualitatively in the text; detailed formulations are Clopay proprietary information.

2: At the same MVTR and same gauge, MDO film gives larger pores and lower MD tear strength.

(SBPP), carded PP, and bicomponent Nonwovens. The microporous film in the composite provides pore sizes much lower than the open areas of the nonwoven for liquid barrier properties and air and moisture breathability. Meanwhile, the nonwoven in the composite provides the cloth-like properties and improved mechanical properties such as improved strength and tear resistance. U.S Pat. Nos. 5,202,173,<sup>(8)</sup> 5,382,461,<sup>(9)</sup> and 5,865,926,<sup>(10)</sup> all assigned to Clopay Plastic Products Company, Inc., reveal the soft film and composite created by the intermeshing process. These novel microporous composites are suitable for disposable hygiene articles and protective health care garment applications. Other special engineering fibers and fabrics can be combined with the novel microporous films described above for many industrial applications as well.

It is worth noting two advantages to microporous composites as described above:

**Composites with fabric provide a cloth-like feel**

One must control the bond strength at the interface between the microporous film and the fabric, no matter what method is used to bond the layers into a composite. If the interfacial bond strength is too high, the resulting composite will feel stiff and unpleasant. If the interfacial bond strength is too low, the resulting composite may delaminate easily during further manufacturing processes or during use by the consumer. Therefore, it is important to control the interfacial bond strength in order to retain the original

characteristics of the film and the nonwoven fabric, which provide barrier properties and the cloth-like feel, respectively. This is particularly important where the film/nonwoven composite is replacing or simulating fabric, such as hygiene or protective garment applications.

**Fabric provides mechanical strength to the composite**

For industrial applications that use film/nonwoven composites, such as carpet backing or building and construction materials, the mechanical strength provided by the fabric in a film/nonwoven composite is very important. The mechanical strength of the fabric provides tear and puncture resistance, while the film provides a moisture barrier and controlled breathability. For these high-strength industrial materials, the interfacial bond between the film and fabric layer must be very high in order to withstand the rougher handling, use, and long-term exposure experienced by the composites in these applications.

**FUTURE PERSPECTIVE**

Calcium carbonate filled polyolefinic microporous films and their composites with lightweight nonwovens are widely used in disposable diapers, hygienic articles, health care products and protective garments. These cost-effective air and moisture vapor breathable materials can be manufactured at high speed on commercial polymer film fabricating equipment. The technology will continue to evolve and be accepted in many other applications and in many other markets. We anticipate:

Table IV.<sup>(1)</sup>  
**General Properties of Microporous Film and Nonwoven Composite**  
**Extrusion Lamination and Intermeshing Process<sup>(2,3)</sup>**

Total Basis Weight (Grams/m <sup>2</sup> )		25	35	50
MVTR (ASTM E96E, g/m <sup>2</sup> /day)		1000-3000	1000-3500	1000-4000
MVTR ( Mocon, 37.8 C, g/m <sup>2</sup> /day)		3000-7000	3000-9000	3000-10,000
Air Flow (cc/cm <sup>2</sup> /min at 90 psi)		200-1200	200-1400	200-1500
Mean Pore Sizes (Microns)		0.07+/-0.02	0.07+/-0.02	0.07+/-0.02
Max. Tensile Strength (N/cm)	MD	4.0-6.5	5.0-7.0	5.5-8.0
	CD	2.0-3.0	2.5-4.0	3.0-5.0
Elongation at Break (%)	MD	100-300	150-300	150-300
	CD	150-450	150-400	150-400

- 1: Film formulations have been described qualitatively in the text; detailed formulations are Clopay proprietary information.
- 2: The properties are very much affected by the type of nonwoven used.
- 3: The properties are very much affected by the bond strength between film and nonwoven.

(A) the continuation of polymeric material development through new polymer catalysts and resin manufacturing techniques. New polymer resins will lead to microporous films and materials that will provide new and improved properties such as elasticity<sup>(27)</sup> and strength;

(B) the continuation of CaCO<sub>3</sub> developments in new coating materials and coating technologies, and in particle size and size distribution control will provide better dispersion and pore size distribution in cavitation processes during the stretching process, which will allow more control over microporous film materials;

(C) the continuation of the development of special fibers and fabrics, which can be used with these novel microporous films for applications in the building and construction market, protective industrial garments and health care products, in the automobile industry, and other applications that are now unimagined;

(D) the continuation of product development in the disposable as well as limited use clothing industry where stretchable and recoverable fabrics using specially engineered fibers combined with these cost effective polyolefin/CaCO<sub>3</sub> microporous films providing waterproofness coupled with air and moisture vapor breathability<sup>(12,13)</sup>;

(E) the continuation of process improvements that will be even more cost-effective in fabricating materials, such as improving the speed and the material efficiency of manufacturing the films and laminates<sup>(11)</sup>;

(F) the continuation of research and development into technology for making air, moisture breathable and biodegradable films and composites for environmentally friendly products<sup>(14,15,16)</sup>;

(G) the further understanding of the mechanisms of pore formation and structure through the three dimensions of microporous films, and how pore formation is affected by film formulations, film-forming techniques, stretching techniques, etc.<sup>(26)</sup>;

(H) the continuation of process developments that allow greater control of the pores sizes and pore size distribution within microporous films, in order to allow precise control of the properties of the microporous film, including the ability to filter and/or prevent the passage of undesired particles, control the breathability of the material, provide 'zones' of variable micropore size, etc.;

(I) the continuing discovery of film additives that improve the properties of the film; prevent the growth of microbes; signal the presence of moisture, chemical fumes, etc. by color changes or other means; and provide other desirable attributes to the film or composite material.<sup>(29)</sup>

Finally, one must pay great attention to intellectual property in this technological area. Since the early publication of patents in Great Britain to W.R. Grace<sup>(19,20)</sup> in 1966 and Yamamoto<sup>(23)</sup> in 1973, more than 250 patents related to microporous films and composites have surfaced globally. It is not the objective of this paper to cover, even briefly, all of these patents. However, one should keep intellectual property considerations in mind when contemplating the manufacture of microporous film products, their composites and their applications.

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#### REFERENCES

- [1] W.L. Gore & Associates, Inc., P.O. Box 1130, Elkton, MD 21912
- [2] Biotex Industries, Inc., 191 Post Road West, Westport, CT 06880
- [3] Cancio et. al, Paper presented at Nonwoven Technology Conference, Sorrento, Italy, March 9-11, 2004, sponsored by Marketing Technology Services, Kalamazoo, MI 49009 USA.
- [4] Barenblatt, G.I. "Methods of combustion theory in the mechanics of deformation, flow, and fracture of polymers." In *Deformation and Fracture of Polymers*, Henning Kaudch, J.A., Hassel, R.J. Jaffee (eds.), Plenum Press (1973), pp. 91-111.

- [5] Cancio et. al., *Nonwovens World*, October-November 2004, pp. 65-77.
- [6] Unpublished Cloday Internal Data.
- [7] U.S. Pat. Pub. 2003/0035943A1, Jones et al., "Multilayer Microporous Films and Methods," 2/20/2003
- [8] U.S. Pat. No. 5,202,173, Wu et al., "Ultra Soft Cloth-Like Embossed Plastic Film Having Post-Embossed Stretched Areas," 4/13/1993.
- [9] U.S. Pat. No. 5,382,461, Wu, "Extrusion Laminate of Incrementally Stretched Nonwoven Fibrous Web and Thermoplastic Film and Method," 1/17/1995.
- [10] U.S. Pat. No. 5,865,926, Wu et al., "Method of Making a Cloth-Like Microporous Laminate of a Nonwoven Web and Thermoplastic Film Having Air and Moisture Vapor Permeabilities with Liquid-Barrier Properties," 2/2/1999.
- [11] U.S. Pat. No. 5,296,184, Wu et al., "Method of Making An Ultra Soft Cloth-Like Embossed Film Having Post-Embossed Stretched Area," 5/22/94.
- [12] U.S. Pat. No. 5,422,172, Wu, "Elastic Laminated Sheet of an Incrementally Stretched Nonwoven Fibrous Web and Elastomeric Film and Method," 6/6/95.
- [13] U.S. Pat. Pub. 2003/0181120A1, Wu et al., "Breathable and Elastic Composite Materials And Methods," 9/25/03.
- [14] U.S. Pat. No. 5,200,247, Wu et al., "Biodegradable Film Containing an Alkanoyl Polymer/PVA Blend and Method of Making Same," 4/6/93.
- [15] U.S. Pat. No. 5,407,979, Wu et al., "Biodegradable Film and Method of Making Same," 4/18/95.
- [16] U.S. Pat. No. 5,851,937, Wu et al., "Cloth-Like Totally Biodegradable and/or Compostable Composites and Method of Manufacture," 12/22/98.
- [17] U.S. Pat. Pub. 2005/0248051, Cancio et al., "Method and Apparatus for Uniformly Stretching Thermoplastic Film and Products Produced Thereby," 11/10/05.
- [18] U.S. Pat. No. 6,811,643, McAmish et al., "Film, Laminated Sheet and Methods of Making Same," 11/2/04.
- [19] British Patent No. 1,044,028, W.R. Grace & Co., "Improvement Relating to Filled Polyolefine (*sic*)," 9/28/66.
- [20] British Patent No. 1,044,502, W.R. Grace & Co., "Stretched Polyolefin Compositions," 10/5/66.
- [21] U.S. Pat. No. 4,153,751, Schwarz, "Process for Stretching an Impregnated Film of Material and the Microporous Product Produced Thereby," 5/8/1979.
- [22] U.S. Pat. No. 4,153,664, Sabee, "Process for Pattern Drawing of Webs," 5/8/1979.
- [23] U.S. Patent No. 3,775,521, Yamamoto et al., "Method of Producing Paper-Like Thermoplastic Synthetic Resin Films," 11/27/73.
- [24] Schwarz, Eckhard C.A., "New Fibrillated Film Structures, Manufacture and Uses," Pap. Synth. Conf. (TAPPI), 1976 (pp. 33-39).
- [25] Japanese Pat. Pubs. J6-2280-234A and J6-2280-235A, Kao Corporation, 5/28/86.
- [26] U.S. Pat. Pub. 2004/015733, McAmish et al., "Method of Analyzing Microporous Polyolefin Film Pore Structure and Three-Dimensional Images Thereof," 8/12/2004.
- [27] U.S. Pat. Pub. 2005/0043460, McCormack et al., "Microporous Breathable Elastic Films, Methods of Making Same, and Limited Use Or Disposable Product Applications," 2/24/2005.
- [28] U.S. Pat. No. 6,013,151, Wu et al., "High Speed Method of Making Microporous Film Products," 1/11/2000.
- [29] Cottrell, S., "Antibacterial Polymer Technology for Nonwovens," presented at INTC 2006, Houston, TX, September 25-28, 2006, sponsored jointly by INDA and TAPPI.

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