

CHEMICALLY-INDUCED HYDROPHILICITY IN  
HYDROPHOBIC POLYOLEFINIC MELT-BLOWN WEBSS. A. Kareem<sup>1, 2</sup>

**ABSTRACT:** Naturally hydrophobic meltblown webs of polyolefinic resins (polypropylene) are rendered hydrophilic using chemical and processing treatments. The level of hydrophilicity is determined to be dependent on additive concentration, introduction method and location. A method devised to measure the treatment durability is found to be exhaustive and able to weed out non-permanently treated webs. FC-171, a fluorochemical surfactant, proved to be the best melt additive at low loading level.

**1.0 INTRODUCTION:** Meltblown webs belong to a group of man-made fibrous materials called nonwoven webs. The term 'nonwoven' itself designates a fabric material produced by methods other than weaving. These materials represent a unique class of fibrous structures. In nonwovens, the fibers are transformed directly into a planar sheet-like fabric structure. This transformation bypasses the intermediate one-dimensional yarn state, that is then either chemically bound or mechanically interlocked (or both) to achieve a cohesive fabric. The paper-making process is a well-known example of a wet-laid nonwoven process using short paper (wood) fibers. Within the plane of a nonwoven material, the fibers may be either completely isotropic or there may be a preferred fiber orientation or alignment usually with respect to the machine or processing direction.

The woven fabric, on the other hand, is usually a planar sheet-like material with pores or holes created by the yarn interlacing pattern (Fig. 1). The dimensions of the fabric pores are usually determined by the yarn structure and dimensions, and by the weaving pattern. Within a given fabric, the pores are reasonably uniform in size and shape. Strength in woven fabric is also directionally dictated. Higher strength and lower extensibility is obtained in the warp direction than in the filling direction. These properties are usually intermediate in the non-orthogonal directions, being dictated by the weaving pattern [1].

Meltblown web made of olefinic polymer was first produced on laboratory scale by Monte [2] in the US Naval Research Laboratory, with the sole objective of generating fine fibers. After Monte's work carried out in the 1950's, the next effort was made by Exxon Corporation, trying to find commercial use for their polypropylene resins. The Exxon work was carried out by Eakin et al [3] in the 1970's. Since then several commercial and research institutions have learned and have been using the technology to produce meltblown webs from polyolefins and other polymeric resins. Although a large number of polyolefins may be extruded into fibers, only polyethylene and polypropylene are extensively used for fibrous applications. Fibers formed from the high-molecular weight isotactic (stereoregular) polypropylene possess good physical properties, adequate thermal stability, as well as the required versatility for various applications.

The meltblown web is formed from entanglement or interlocking of molten filaments before they get cooled to ambient condition. The degree of bonding or interlocking has a crucial effect on the final properties of the nonwoven material. In general, strength increases, softness decreases, extensibility decreases, and optive capacity decreases with increasing degree of bonding or interlocking [4].

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limited to the hopper; in the extruder, screw slippage was experienced at additive level beyond 2%. The blends had to be pushed through the hopper with the aid of a push-rod and this correspondingly resulted in pressure swings in the extruder and, hence, non-uniform basis weight distribution in the extruded meltblown webs collected.

**2.2 Method 2:** Another method attempted to incorporate the surfactant melt additives into the web was to pump the liquid additives into the bottom of the hopper, directly on top of the extruder screw using a peristaltic pump as shown in Fig. 2. This had an advantage over method 1 of preventing resin bridging in the hopper. At blend levels of the surfactant over 2%, pressure swing-related problems were experienced in the extruder and subsequently in the meltblown webs collected.

**2.3 Method 3:** The melt additives were pumped at high pressure into the metering section of the extruder as shown in Fig. 2. This method had the advantage of minimizing additive decomposition and greatly reducing the pressure swing syndrome. However, additional mixing (static mixer) was required to obtain homogeneous mixing of the additives in the molten resin. A Ruska pump was used, and liquid surfactant loading up to 4% was possible.

**2.4 Method 4:** Cascade extrusion set-up was used to achieve liquid surfactant loading up to 20% (Fig.3). A Zenith pump was used to meter the surfactant into the metering section of the first extruder; the effluent of the first extruder was then fed into the metering section of the second extruder. This process configuration gave a good mixing and was capable of handling up to 20% liquid surfactant level in the meltblown webs.

**2.5 Method 5:** The method employed commercially and in most research laboratories commonly are various forms of topical treatments whereby untreated meltblown web is either sprayed with the surfactant solution, or dipped in solution. As will be mentioned later, this is the least effective of all the methods tried for incorporating hydrophilic property to meltblown web durably.

**2.6 Hydrophilic Treatment Explanation:** After producing webs into which surfactants have been incorporated, a test for wettability, or more precisely the durability of treatment, has to be chosen. The meltblown webs once treated with surfactant fall into absorbent material classification. With respect to fluid flow, absorbent materials are usually porous media with structures highly complex to describe. The pore sizes are different and are three-dimensionally interconnected, so that even the one-dimensional fluid flow actually follows tortuous paths, rather than straight lines as in capillary tube flow. Also due to the different pore sizes, the fluid located at partially saturated regions will experience a multitude of different "pulls" from different pores. The pore structure of the absorbing medium therefore significantly influences the fluid flow process.

To describe fluid flow, Darcy's law describing fluid flow kinetics through porous media in terms of the driving force gradient and medium permeability could be used. The Kozeny-Carman and Iberall approaches could also apply. The problem is however not a steady-state type; so these laws would not correctly represent the unsteady state [6,7]. In most practical absorbency cases, the liquid movement is an unsteady state flow, where the porous medium is not uniformly and completely saturated. The liquid distribution throughout the medium changes with time.

At any given time, as liquid is absorbed into a porous medium, there is a saturation gradient in the medium along the direction of flow and this saturation gradient changes with time as the absorption process continues [8]. A saturation rate equation of this form (combining the law of mass conservation and differential Darcy's equation) applies:

$$\frac{\partial s}{\partial t} = \frac{\partial}{\partial x} \left[ \frac{F(s)}{s} \frac{\partial s}{\partial y} \right]$$

where  $F(s)$  is the diffusivity factor, referred to in soil physics as "moisture diffusivity",  $x$  is the flow direction, and  $s$  is the surface area of the matrix flow channel.

The solution to this generalized equation describes the unsteady state flow behavior in porous media in terms of saturation profiles along the length of the sample at various times. Since  $F(s)$  is not constant however, numerical methods are needed to solve the equation [9].

Induced Hydrophilicity in Meltblown Webs



Figure 1a

Figure 1a - Scanning electron photomicrograph of cotton fibers. [111]

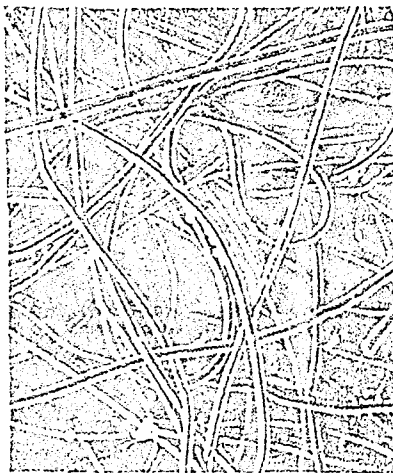


Figure 1b

Figure 1b - Scanning electron photomicrograph of polymeric fibers on fabric. [111]

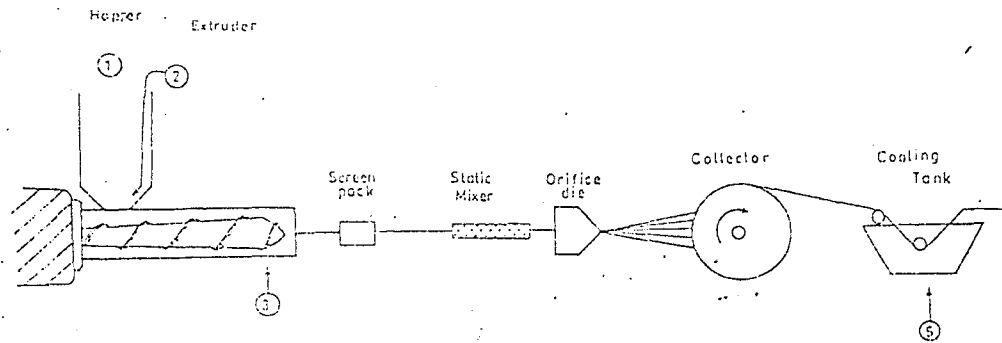


Fig 2 Equipment layout for Surfactant Incorporation into Meltblown webs

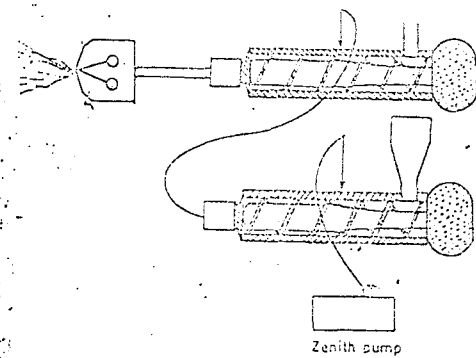


Fig 3 Schematic diagram of the cascade extrusion

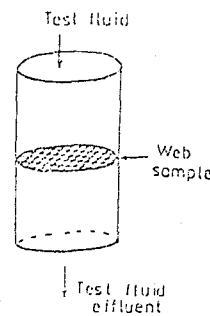


Fig 4 Schematic diagram of the flux test

In practical terms, the significant factors affecting this unsteady flow are:

- **Gravity:** For both upward and downward movement of fluid, the importance heightens at large periods of time from flow onset.
- **Initial moisture:** It has been found that liquid penetration into a porous medium is faster when the medium contains some initial moisture than when completely dry.
- **Dimensional changes:-** There is an associated dimensional change of the porous medium bulk volume when a liquid is imbibed. Depending on the nature of the porous material there can be either a collapse or swell when wetted.
- **Transient behaviour of sub-second time:** Because the saturation rate equation above fails to account for kinetic and other energy loss terms, it is not applicable when studying the transient flow behaviours at sub-second times from the initial time [10].
- **Structural factors:** The effect of pore structure quality in terms of pore connection, continuity of the pore size distribution, and microscopic homogeneity of the pore structure also must be accounted for in considering the unsteady state flow.

There are many studies reported in the literature on the rate at which liquid is absorbed and retained in porous media. Most of these tests are based on American Standards of Testing Materials (ASTM), Technical Association of Pulp and Paper Industries (TAPPI) standard methods, and various other standard testing manuals. These techniques of absorbency measurement are all designed to determine the amount of liquid absorbed. In some tests, the spacial advances of the liquid are monitored. Overall, the techniques either measure spontaneous (demands) liquid absorption or liquid retention. In other words, all the tests measure the equilibrium absorbency reached from dryness or by exsorption from saturation.

These tests are useful in R&D screening exercises, but fail to meet the practical and rigorous requirements of commercial end-user specifications. It is on this basis that the flux test used to screen the meltblown webs is formulated. Data obtained in the flux test accounts for the non-steady nature of the fluid flow and the five factors enumerated above. The test gives a uniform yardstick for evaluating the web samples.

For a customer, a durable wipe is supposed to stay hydrophilic for a reasonable number of wetting cycles. The rate of absorption of the fluid becomes secondary. The contact angle and liquid/vapour pressure relationship are of no consequence to a mother whose baby rewets the diaper. The ability of an hydrophilic web to allow fluid passage becomes the only issue considered important. Because the flux test uses the same amount of fresh fluid each time a sample is subjected to the test, a lot of factors are normalized. The time for the measured liquid to flow through gives an indication of the retention or loss of the hydrophilicity by the web. Unless a web sample is "visibly" porous, the test is able to retain fluid or screen out an hydrophobic sample easily. The amount of fluid engaged is not enough to effect flow due to gravitational influence only. In other words the way the flux test is run, when there is a rapid desorption of surfactant treatment, subsequent rewetting by fresh fluid becomes impossible.

In carrying out the flux test (Fig.4), the web sample is held tightly in-between a bi-level open-ended cylinder such that  $66\text{cm}^2$  of the web sample is exposed.  $200\text{cm}^3$  of aqueous fluid is poured on the side of the cylinder onto the top of the web. The time taken for the liquid to wick through the web is noted. The test sample is removed and allowed to dry overnight. The test is repeated on the same sample with fresh aqueous fluid over a period of seven days or until the web stops wetting due to the loss of the hydrophilic treatment.

**3.0 RESULTS:** The objective of this study was to find the most practical means of impacting durable hydrophilic property to polypropylene meltblown webs. In the investigation, various commercially known surfactant rewetting agents were tried, as either topical treatment or melt-additive (injection and cascade runs) or both. Most of the

topical treatments gave products that at best can only be reused once, making these products most applicable as disposables. Bringing product economy into the picture, any surfactant rewetting agent has to give the desired level of durability in the webs at blend levels equal to, or lower than, 1%.

As melt additives, five surfactant rewetting agents were tried; they are polyethylene glycol-monolaurate (PEG-ML 200); Triton X-100, Triton X-102, Triton X-405 (non-ionic surfactants based on polyethylene oxide-alkylphenol chemistry); and FC-171 (a fluorochemical rewetting agent). Table 1 summarizes the results obtained while Table 2 summarizes the results for the cascade runs. Table 3 summarizes the results for the topical treatment accomplished by dipping meltblown web in aqueous solutions of the respective surfactants.

**4.0 DISCUSSION:** The first point to be made is that from the results depicted in the three tables FC-171 is, by far, more active and more durable than the other rewetting agents in whichever way it is incorporated to the meltblown web. There is no doubt that the temperature history in the extruder has some influence on the effectiveness of all the rewetting agents. But it becomes obvious, when one compares the level of effectiveness achieved in topical treatment with those of others where high temperature extrusion conditions are experienced, that addition of the surfactant in the melt provides superior activity to the topical treatment. By comparing Tables 1 and 2, it can be inferred that the melt mixing achieved in methods 2 and 3 may be insufficient when corresponding levels of additives are compared with method 4. In method 4, the melt additives are introduced into a molten polymer, and

with the aid of the cascade arrangement better mixing of the additives and the molten polymer is achieved. It can be inferred that method 4 is superior to other methods of incorporating additives into meltblown web; it must, however, be pointed out that it is clearly more difficult to run as a process method than the other methods.

No mention is made of data from method 1 because non-uniform web samples were collected. The level of additive incorporation varied from sample to sample, as a consequence of hopper resin bridging and screw slippage.

This study confirms the ability of the rewetting agents to be incorporated into topically treated web. At best though, the samples made using topical treatment can be considered non-permanent. Products from topical treatment will only therefore meet the required standard for disposable applications. For the topical treatment, FC-171 proved better than Triton X-100. A water soluble polymer,

Table 1. Effectiveness of various surfactant rewetting agents as melt additives

	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	
a PEG-ML 200	1%	Non-wetting						
	1% (annealed)	Non-wetting						
	5%	25s	155s	191s	205s	>300s	>300s	>300s
	5% (annealed)	13s	Non-wetting					
b Triton X-100	0.5%	Non-wetting						
	0.5% (annealed)	3s	58s	80s	>300s	Non-wetting		
	1%	68	>300s		Non-wetting			
	1% (annealed)	4s	45s	52s	>300s	Non-wetting		
c Triton X-102	0.5%	Non-wetting						
	0.5% (annealed)	2s	70s	80s	>300s	Non-wetting		
	1%	300s	Non-wetting					
	1% (annealed)	10s	116s	125s	>300s	Non-wetting		
d Triton X-405	0.5%	Non-wetting						
	0.5% (annealed)	Non-wetting						
	1%	Non-wetting						
	1% (annealed)	Non-wetting						
e FC-171	0.5%	6s	14s	75s	217s	>300s	>300s	>300s
	0.5% (annealed)	5s	20s	22s	40s	44s	75s	114s
	1%	4s	5s	12s	48s	52s	70s	70s
	1% (annealed)	5s	38s	59s	105s	150s	260s	>300s

Table 2. Results for the cascade runs

a	PEG-ML 200	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	3.00%	Non-wetting						
	6.40%	2s	2s	2s	2s	2s	2s	2s
	9.96%	2s	15s	22s	39s	57s	58s	58s
b	Triton X-100	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	2.0%	Non-wetting						
	4.0%	24s	42s	71s	>300s	Non-wetting		
	4.5%	2s	3s	5s	9s	14s	42s	105s
	7.7%	2s	3s	3s	4s	4s	10s	22s
	11.8%	2s	2s	2s	3s	3s	3s	4s
	13.6%	1s	2s	2s	2s	2s	2s	3s
c	FC-171	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	0.5%	2s	12s	16s	21s	22s	30s	27s
	0.8%	2s	2s	2s	2s	3s	3s	3s
	2.0%	2s	2s	2s	2s	2s	2s	2s
	4.0%	2s	2s	2s	2s	2s	2s	2s
	5.0%	1s	1s	1s	1s	1s	1s	1s
	11.4%	1s	1s	1s	1s	1s	1s	1s

Table 3. Effectiveness of various surfactants, applied topically

Surfactant	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
0.5% FC-171	19s	32s	58s	>300s	>300s	>300s	>300s
0.5% Triton X-100	32s	Non-wetting					
1.0% FC-171	19s	16s	39s	120s	120s	162s	258s
1.0% Triton X-100	62s	110s	Non-wetting				
4.0% Polyvinyl alcohol	300s	300s	>300s	>300s	>300s	>300s	>300s

annealed webs fail to meet the flux test durability standard or in other words the rewetting ability is lost after few fluid contacts. Last but not the least, this study suggests that there may be a critical loading factor for some rewetting agents in the web. Looking at the data of Tab 2a especially, at higher level of loading, treated web seems to be losing its hydrophilicity faster. This further emphasizes the importance of anchorage of the surfactant molecules to the meltblown web matrix. At higher loading, higher monolayer overturning and desorption is experienced, pointing out the fact that for each surfactant the maximum loading has to be determined for the method of incorporation utilized.

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polyvinyl alcohol (PVA) dissolves in water at 4% level and when topically applied produced a "permanent" treatment to the web, albeit with longer fluid retention times. PVA when incorporated into the web cakes on drying, thereby "plugging" some pores.

As earlier noted, the loading of surfactants at levels higher than 1% may not be economically justifiable. However, the cascade method proved that high levels of fluid can be incorporated into the melt region of meltblown process. The processing problem of screw slippage is not experienced because the fluid is introduced where or after all the solid resins have melted. The benefit to be realised from this process success is that expensive compounding of liquid additives may not be necessary if this cascade method can be implemented to introduce additives into the meltblown materials.

In most of the rewetting agents studied, enhanced activity was witnessed when web samples were annealed between hot rolls. This could be attributed to blooming process whereby more lyophilic ends of the surfactant molecules are exposed. It can be further inferred that such molecular rearrangement weakens the bonding of the surfactant molecules to the web. Most