LIQUID INTERACTION IN CELLULOSE-CONTAINING FIBROUS STRUCTURES

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Abstract

Liquid wetting and transport in a porous medium is governed by the properties of the liquid, liquid-medium surface interaction, and geometrical configurations of the porous medium. This paper describes the principles and methods of quantifying the wetting and transport properties of water in several fibrous structures. The water wetting contact angle and retention of woven and nonwoven cotton, cellulose filter, and other cellulose-containing materials are reported.

Introduction

Liquid transport in a fibrous medium is preceded by liquid wetting of the fibers. Wetting of a fiber is determined by the fiber surface properties and the liquid's properties. The manner in which the liquid is transported through the porous medium depends on the capillary forces in the pore structures. Capillary action is governed by the properties of the liquid, the fiber surface wetting characteristics, and the geometrical configurations of the porous medium. Liquid properties, such as surface tension, viscosity, and density, as well as the surface wetting forces of fibers can be experimentally determined. The pore structure of a fibrous medium is, however, complicated and much more difficult to quantify.

Wetting Contact Angle of Single Fibers
Wetting force (F_w) of a fiber can be measured by immersing it vertically into a liquid:

$$F_w = p \, \gamma \, \cos\theta \qquad \text{eq. 1}$$

where p is fiber perimeter, γ is liquid surface tension and is θ the liquid-fiber contact angle. The value of p can be estimated from the measurement in a total wetting liquid, such as hexadecane, where cosine θ is 1:

$$p = F_w / \Upsilon \qquad \text{eq. 2}$$

With the derived p value, the wetting property of a fiber can be described by the contact angle with a liquid of known surface tension γ:

$$\theta = \cos^{-1} (F_w / p \, \gamma) \qquad \text{eq. 3}$$

Wetting Contact Angles of Porous Materials
Surface wettability of porous materials can also be measured. The simultaneous measurement of liquid wetting and wicking in fabrics has been described using an electronic microbalance (Hsieh et al 1992, Hsieh 1995). The manner this measurement is conducted is similar to that of a single fiber, i.e., by connecting a vertically hung fabric to a microbalance, raising a liquid upward to contact the lower end of the material, and allow wetting and wicking to occur. When wetting and wicking stop changing or reach the steady-state, the balance reading (ΔB_{st}) is the sum of the external wetting force (F_w) and the internal liquid rise (W_t):

$$\Delta B_{st} \, g = F_w + W_t \, g \qquad \text{eq. 4}$$

The contribution of Fwo or Wt to the balance detection (ΔB_{st}) depends upon the wetting properties and the porous structure of the material. The external wetting force is, however, not affected by the capillary length.

After reaching steady state, the material is removed from water. The balance reading following separation from liquid (ΔB_{sp}) gives the mass of liquid retained in the capillary (W_t):

$$\Delta B_{sp} = W_t \, g \qquad \text{eq. 5}$$

Wetting force of the fabric surface (F_w) can be decoupled from the liquid retention component of the measurement:

$$F_w = (\Delta B_{st} - \Delta B_{sp}) \, g$$
$$= \gamma \, p \, \cos \theta \qquad \text{eq. 6}$$

where p is the fabric-liquid interfacial dimension or perimeter of the material and qo is the external liquid-solid contact angle. The external perimeter is derived by measurements in hexadecane similar to the single fiber derivation (eq. 2). The p value is calculated from the difference between ΔB_{st} and ΔB_{sp} values in hexadecane:

$$p = (\Delta B_{st} - \Delta B_{sp}) g / \gamma \cos \theta \qquad \text{eq. 7}$$

With derived P and F_w values, the liquid-fabric contact angle can be calculated the same way as with single fibers (eq. 3).

The wetting characteristics of cotton fabrics have been found not to be affected by their configurations, including fabric length, fabric-water interface depth, and fabric direction and fabric width (Hsieh et al 1992). The cosine contact angles obtained on the woven structures including 100% cotton, polyester, Nomex, acetate, and rayon fabrics are the same as those obtained from their constituent single fibers. These experimental results demonstrated that surface wettability of any fabric containing a single fiber type is identical to the wettability of its constituent single fibers. In addition to being a straightforward method of deriving fabric wetting contact angles, measurement in the fabric form offers the advantage of simultaneous detection of dynamic liquid transport and retention information.

Liquid Transport and Retention of Porous Materials
Liquid transport properties of a porous medium are determined by its geometrical configuration, which is complex and difficult to quantify. The pore structures in fibrous materials depend significantly on the methods of assembly and fiber types. In woven fabrics, liquid movement is directed along the warp, filling, and, to a lesser degree, the thickness direction of the fabric. The yarn structure and the yarn density in the fabric therefore determine the fabric pore structure. In nonwoven structure, directions of liquid movement may not be as distinct as in the wovens because of the absence of yarn structure. The nonwoven pore structure is determined by the manner by which fibers are assembled together. Fiber width, length, and shape, as well as fiber alignment influence the pore sizes, distribution of pore sizes, and other quality of the capillary channels such as pore connectivities.

Quantitative prediction of liquid transport phenomena in fibrous materials can be challenging because of their complex pore structure and sometimes altered properties when interacted with the liquid. The variation and distribution of pores lead to preferential liquid movement toward smaller pores resulting in partial draining of previously filled pores in the fibrous structure. The dynamic movement of liquid can cause fiber shifting and changes in the non-rigid fibrous structure. Changes in fiber properties when wet by the liquid can significantly affect the liquid movement and retention properties. Fiber swelling not only increase liquid retention in the fibers at the expense of the capillary liquid capacity in inter-fiber pores but

also complicates the pore structure. Reduction in wet fiber strength and resiliency can lead to collapse of pores and lowering of the liquid holding capacity.

This paper describes and discusses the measurements of the liquid wetting and transport properties of several nonwoven and cellulose-containing materials.

Experimental

The nonwoven materials studied include cotton and aramide nonwovens and glass and cellulose filter paper. The cotton nonwoven was formed by carding and crosslapping of 1.1 inch staple and hydroentangled (Cotton Incorporated). The cotton nonwoven was bleached with hydrogen peroxide and finished with butoxyethyl stearate finish. The glass filter was made of inert borosilicate glass and did not contain organic binders (G6 grade from Fisher Scientific). The cellulose filters were qualitative grade Whatman #1 and #2 from Fisher Scientific. The weight and thickness of these nonwovens were characterized by ASTM method 1910. Ten specimens were used for each of the measurements.

Measurements of wetting and transport properties of these materials were performed following a previous procedure (Hsieh et al 1992, Hsieh 1995). The nonwovens were cut into 0.635 cm wide and 2.54 cm length strips with a die cutter. Water wetting contact angle and fiber perimeter measurements were also performed on single fibers sampled from some of these materials using a method previously reported (Hsieh et al 1992). All samples were measured without further cleaning unless specified and conditioned at 20°C and 65% relative humidity prior to the wetting and wicking measurements.

Results and Discussion

The water wetting contact angles of the nonwovens were derived (Table I). Sampling of single fibers was attempted on all nonwoven materials but was only successful on the aramid nonwoven. The fibers taken out of the cellulose and glass filters were too short for single fiber wetting measurements whereas considerable damage was observed on the cotton fibers separated from the hydroentangled cotton nonwoven. Therefore wetting contact angle comparison between nonwoven and single fibers was made on the aramid. The average single fiber water wetting contact angle of the aramid was similar to that derived from the nonwoven form (Table II). The similarity in water wetting contact angles between single fibers and their woven fabric has been reported on nylon 66 and Nomex (Hsieh et al 1992). The current data is consistent with our previous observation. Although the exact composition of the aramid nonwoven is not know, its fiber and bulk contact angles appear to be close to that of the Kevlar 49 (Hsieh et al 1991).

Surface wetting behavior of any material can significantly influenced by what is on the surface. Since the hydroentangled cotton nonwoven was finished with butoxyethyl stearate, the effects of cleaning by several solvents were evaluated (Table III). Carbon tetrachloride improves the wettability of the cotton nonwoven, but neither alcohols influence the water wetting contact angles. The water wettability of this nonwoven cotton is considerably better than the raw (unscoured) cotton, but not as low as those of scoured and/or bleached cotton. Water contact angles of the raw cotton fibers and unscoured fabrics have been reported to be 93.9° ($\pm$3.3°) and 95.3° ($\pm$19.4°), respectively (Hsieh, 1992). Commercially and laboratorily (2 hours in boiling 3% NaOH) scoured cotton fabrics lowered the water contact angles to 41.5° ($\pm$3.2°) and 41.3° ($\pm$5.4°) (Hsieh et al 1996). Bleaching with either NaOCl or H2O2 of the laboratory scoured cotton further reduced its contact angle to about 36°. Bleaching without prior scouring of this nonwoven explains its wetting behavior.

Comparison Among Nonwovens

The nonwoven materials have wide ranged weight and thickness (Table I). The cotton nonwoven is highest in both weight and thickness whereas the aramid nonwoven has the lowest weight and the cellulose filters have the lowest thickness. From the weight and thickness values, nonwoven bulk density (g/cm^3) can be calculated

$$\rho_b - = \frac{\text{Fabric weight } (g/cm^2)}{\text{Thickness (cm)}} \qquad \text{eq. 8}$$

When fiber density is taken into consideration, the overall porosity (f) of a porous material can be described as

$$\phi = 1 - \frac{\rho_b}{\rho_f} \qquad \text{eq. 9}$$

where ρ_b and ρ_f are the nonwoven bulk and fiber density, respectively. Maximum absorption capacity (C_m) is the weight ratio of the absorbed liquid over the dry solid medium weight, g/g

$$C_m = \frac{\rho_l}{\rho_b} \bullet \frac{\phi}{1-\phi} \qquad \text{eq. 10}$$

where ρ_l is the liquid density. Fabric bulk densities range from 0.064 g/cm^3 of the aramid nonwoven to 0.478 g/cm^3 of the cellulose filter. Fabric porosity was over 0.9 except for the cellulose filter.

The maximum absorption capacity (C_m, ml/cm^3) can be calculated from porosity and fabric thickness. Experimentally, liquid absorption capacity in a vertical fabric can be estimated by measuring the uptake of a liquid with low surface tension, density and viscosity, such as hexadecane. The measured liquid C_m, of cotton nonwoven is close to the high value of the calculated C_m, whereas those of other nonwovens are below even the lower calculated values. This is attributed to the differences in the compressiveness of these nonwoven.

The other major effect, i.e., surface chemistry, can be demonstrated by our previous work on alkaline scouring and enzymatic scouring on cotton fabrics (Hsieh et al 1996, Hsieh et al 1999). When fiber contents are different, two nonwovens with similar structure and geometric configurations can have distinctly different pore structures. The strong effect of fibers on fabric pore structure can be illustrated by these fibrous materials studied.

These discussions illustrate that the mass transport data provide the valuable information on the pore area responsible for actual liquid transport at specific distance from the liquid source. These approaches quantify actual liquid wetting and transport in woven fabrics and have potentially useful for other non-rigid pore structures

Summary

For a fibrous material to effectively transport a liquid, the fibers must be easily and thoroughly wetted by the liquid. The inter-fiber pores must have the proper dimensions to produce sufficient capillary pressure, inter-connective pathways to transport the liquid, and overall porosity to retain the liquid. Capillary theory shows that smaller pore sizes produce higher capillary pressure and thus enhance liquid spreading distance. The capacity of a fibrous material to retain liquid, on the other hand, is determined not only by its pore sizes but also its overall porosity. Optimal absorbent performance, whether measured by the travel distance of liquid spreading or total liquid retention, can be achieved by controlling the pore sizes and their distribution. The distance of liquid advancement is greater in a smaller pore because of the higher capillary pressure, but the mass of liquid

retained in this pore is also small. Larger mass of liquid can be retained in larger pores, but the distance of liquid advancement is limited. Therefore, fast liquid spreading in fibrous materials is facilitated with small, uniformly distributed and interconnected pores whereas high liquid retention can be achieved by having a large number of such pores or a high total pore volume.

This paper describes an experimental method for determining the liquid wetting and transport properties of nonwovens. Water transport and absorbency in a fibrous material are dependent upon the fiber-water interaction and the geometrical configuration of the fibrous material. Changes to either component result in changes to liquid transport and absorbency in the material. Due to the complexity of the wetting and wicking phenomena, separating the surface wetting and pore geometry contributions is critical to the design and evaluation of new fibrous structures. The experimental and data derivation approaches described in this paper demonstrate that the wetting and wicking components of a porous medium-liquid pair can be individually identified. Together with other physical measurements, this capability of differentiating wetting and wicking is useful in facilitating the development of fibrous structures with specified absorption properties via new materials and processing technologies.

References

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Table I. Water contact angles of nonwovens.*

	Nonwoven n	θ, degree
Cotton	5	54.2 (+4.0)
Cellulose	5	28.3 (+1.8)
Glass	7	27.2 (+6.0)
Aramid	3	64.5 (+4.9)

* All samples were used as is without further cleaning.

Table II. Water contact angles of polyamide structures.*

	Single Fiber		Woven/Nonwoven	
		θ		θ
	n	degree	n	degree
Aramid[1]	15	61.2	3	64.5
		(+4.4)		(+4.9)
Nylon[2]	4	61.4	4	57.4
		(+2.9)		(+4.1)
Kevlar[3]	6	64.6	-	---
		(+1.9)		
Nomex[2]	3	54.8	4	57.5
		(+5.2)		(+4.7)

* The aramid nonwoven was used without further cleaning. Other samples were cleaned in tricholoro-triflouro-ethane before measurements.
Numbers denote the forms of original materials: 1nonwoven, 2woven, 3 filament.

Table III. Water contact angles of hydroentangled cotton nonwoven.

Cleaning agent	n*	θ
none	9	59.8 (3.2)
methanol	9	58.8 (7.2)
ethanol	6	57.1 (2.0)
CCl_4	5	54.2 (4.0)

* number of measurements.

Table IV. Liquid retention properties of nonwovens.

Properties	cotton	cellulose	glass	aramid
Fabric weight, mg/cm^3				
	11.20	9.66	5.51	3.56
	(0.02)	(0.13)	(0.05)	(0.05)
Fiber thickness, mm				
P=0 g/cm^2	747	202	481	559
	(12)	(15)	(5)	(114)
P=70.7 g/cm^2	572	177	376	410
	(12)	(15)	(3)	(5)
ρ_b, g/cm^3	0.150	0.478	0.115	0.064
ρ_s, g/cm^3	1.54	1.54	2.50	1.40
Porosity	0.90	0.69	0.95	0.95
Calculated[a] C_m, $\mu l/cm^2$				
low	4.5	1.2	6.4	10.8
high	6.0	1.4	8.3	15.0
Measured C_m, $\mu l/mg$				
	5.62	1.07	6.07	9.44
	(0.36)	(0.04)	(0.15)	(0.82)
Measured water C_m, $\mu l/mg$				
	5.98	1.87	8.52	1.40
	(0.31)	((0.06)	(0.16)	(0.23)
C_m ratio, water/capacity				
	1.1	1.6	1.4	0.15
	(0.02)	(0.03)	(0.04)	(0.03)
Water contact angle, degree				
	54.2	28.7	27.2	64.5

a The high and low liquid retention capacity C_m values are calculated from thickness measured under pressure at 0 and 70.7 g/cm^2, respectively.