

Sorption and Vapor Transmission Properties of Uncompressed and Compressed Microcellular Starch Foam

GREGORY M. GLENN,^{*,†} ARTUR P. KLAMCZYNSKI,[†] GARY TAKEOKA,[†]
WILLIAM J. ORTS,[†] DELILAH WOOD,[†] AND ROBERT WIDMAIER[‡]

Western Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture,
USDA-ARS, 800 Buchanan Street, Albany, California 94710, and Widmaier Consulting,
20123 186th NE, Woodinville, Washington 98072

Microcellular starch foams (MCFs) are made by a solvent-exchange process and consist of a porous matrix with pores generally ranging from $\sim 2 \mu\text{m}$ to submicrometer size. MCF may potentially be useful as a slow-release agent for volatile compounds because of its ability to sorb chemicals from the atmosphere and to absorb liquids into its porous structure, and because it can be compressed to form a starch plastic. MCF made of high-amylose corn and wheat starches was prepared with or without 2% (w/w) silicone oil (SO) or palmitic acid (PA). The MCF was loaded with 1% of various volatile compounds with vapor pressures ranging from 0.02 to 28 mm. The MCF depressed the vapor pressure from 0.37 to 37% compared to a control containing no MCF. Incorporating SO or PA in the matrix of the MCF had little effect on sorption of volatiles. Compressing MCF at 1.4, 6.9, and 69 MPa made a starch plastic with varying porosity. The vapor transmission rate of various volatile compounds through MCF was positively correlated to the vapor pressure of the test compound but was inversely proportional to the compression force used to form the starch plastic. The results indicate that uncompressed and compressed MCFs could be effective slow-release agents for a variety of volatile compounds, especially if used together.

KEYWORDS: Starch; microcellular foam; starch plastic; sorption; vapor transmission; volatile compounds; encapsulation

INTRODUCTION

Effective slow-release agents for dispensing agricultural chemicals are needed to minimize the amount of chemicals applied to crops, lower costs, reduce the risk of human exposure, and lessen the environmental impact associated with their use (1). Slow-release agents can also improve the efficiency of chemical applications by minimizing losses due to volatilization, leaching, and light decomposition (1, 2). Starch products have been used to encapsulate a host of flavor compounds because of their low cost, bland taste, and stable supply, and because they afford protection to unstable compounds (3). Hydrolyzed starches and modified starches are among the main carriers used commercially for flavor encapsulation (3, 4). Flavor compounds are primarily encapsulated by spray-drying or extrusion processes (3, 4).

Starch has also been explored as a slow-release agent for agricultural chemicals because of its degradability in many agricultural environments and versatility in processing. Carr et al. (5) encapsulated an active herbicide in a starch extrudate. The extrusion process subjected the encapsulated compound to

temperatures in excess of 100 °C and is therefore not a process that can be used with compounds that are not thermally stable. Wing et al. (1) encapsulated a herbicide in a pearl corn starch melt prepared by jet cooking. The starch melt was formed at 143 °C and then cooled to 93 °C before the compound was mixed into the starch melt. The melt was cooled to 4 °C to promote retrogradation of the starch, dried, and finally ground to the desired particle size. In yet another approach, McGuire et al. (2) chemically linked a herbicide to pregelatinized starch as a means of controlling the release of active ingredient.

Glenn and Irving (6) described a process for making a food-grade starch-based microcellular foam (MCF). The MCF was composed of an open matrix of pores generally smaller than 2 μm , with some pores in the range of 5–14 Å. The MCF could be formed into sheets of varying thicknesses or beads of varying diameters (7). Buttery et al. (8) later showed that wheat starch MCF beads effectively sorbed various volatile compounds in a way similar to other microporous foams, such as charcoal. The sorption occurred at room temperature, which made the process compatible with heat-labile volatile compounds. The use of MCF as an alternative to traditional spray-drying or extrusion processes to effectively encapsulate flavor compounds was proposed (8).

* Corresponding author [telephone (510) 559-5677, fax (510) 559-5936, E-mail gmg@pw.usda.gov].

[†] USDA-ARS.

[‡] Widmaier Consulting.

Dispensing agents have been developed for the slow release of volatile insect pheromone compounds to control agricultural pests (9). Pheromone compounds are effective in small concentrations and may be applied as concentrated aerosols by intermittent sprays from microjets, encapsulated in emulsions and applied as a spray, impregnated into paraffin disks or poly(vinyl chloride) spirals that are placed in the field, or dispersed by various other means (10–12). Some application methods have advantages over others, but each method may serve a niche need. The use of MCFs for slow/controlled release of volatile agricultural chemicals could be of commercial interest since starch MCFs are safe (food grade) and biodegradable, and they sorb volatiles that can be released when the MCF microstructure is disrupted by water absorption. MCFs can be loaded with oils or fats to provide a lipid phase that may improve the sorption of nonpolar compounds. The MCF may also be compressed into a sheet of starch that has the appearance and some mechanical properties comparable to those of commercial plastics (13). The starch plastic could be used to form an additional barrier to diffusion of volatile compounds. The present study was initiated to determine the sorptive properties of starch MCFs with select flavor and pheromone compounds, investigate whether loading an oil or fatty acid compound to the MCF affects sorption, and evaluate the vapor transmission properties of uncompressed and compressed starch MCFs.

MATERIALS AND METHODS

Materials. Unmodified wheat starch (Midsol 50) was obtained from Midwest Grain (Topeka, KS). Unmodified, high-amylose corn starch (Hylon VII) was purchased from National Starch (Berkeley, CA). Silicone oil (CAS Registry No. 63148-62-9), palmitic acid (CAS Registry No. 57-10-3), (*S*)-(-)-limonene, 3-pentanone, 3,5-lutidine, 3-methyl-2-cyclohexen-1-one (Douglas fir beetle pheromone), and 9-decen-1-ol (similar to one of the pheromones for peach twig borer) were purchased from Sigma-Aldrich Corp. (St. Louis, MO). Ethyl (*E,E*)-2,4-decadienoate (bartlett pear odor) and (*E*)-5-decen-1-yl acetate (peach twig borer pheromone) were purchased from Bedoukian Research Inc. (Danbury, CT).

Microcellular Foam. High-amylose corn starch (HACS) microcellular foam was prepared by heating an 8% (w/w) aqueous starch slurry to 140 °C in a pressure reactor (Paar Instrument Co., Moline, IL), cooling the slurry to approximately 90 °C, and injecting it in chilled oil (5 °C) to form small beads (1 mm diameter). The beads were rinsed in hexane to remove residual oil and dehydrated in a graded ethanol series (40, 70, and 90% and three changes of 100% ethanol). The beads were transferred to a bomb, equilibrated with liquid CO₂, and then critical point dried to form MCF beads. The physical and mechanical properties of HACS MCF have been described elsewhere (6).

Wheat starch MCF sheets were prepared by stirring and heating an 8% aqueous slurry to 90 °C and maintaining the temperature for 30 min. The starch melt was poured into sheet molds (33 × 42 × 0.7 cm) and kept in a refrigerator overnight. The sheets were removed from the molds and equilibrated in a graded ethanol series (40, 70, and 90% and three changes of 100% ethanol) to displace the water. Wheat starch MCF was made by simply evaporating the ethanol from the sheets in a stream of dry nitrogen gas. The MCF sheets were approximately 0.45 cm thick and were stored in plastic bags for later use.

Infusion of MCFs with Palmitic Acid (PA) and Silicone Oil (SO). Some wheat starch MCF samples were infused with PA or SO to determine whether sorption of hydrophobic chemicals could be increased beyond levels in MCFs without PA or SO. The HACS MCF samples could not be infused with solvents without the MCF collapsing and were thus not tested. A stock solution of PA in ethanol was prepared by stirring 1.0 g of PA into 99 g of absolute ethanol and heating for 30 min in a water bath (60 °C). A stock solution of SO was made by dissolving 1.0 g of SO in 99 g of petroleum ether at room temperature. Samples (0.5 g) of wheat starch MCF were infused with PA or SO by placing 1 g of solutions containing either PA or SO on the MCF surface.

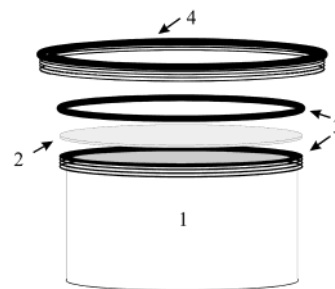


Figure 1. Illustration of diffusion cell used in determining vapor transmission rate (VTR) of test compounds through a starch membrane made of microcellular foam (MCF) or MCF compressed at 1.6, 6.9, or 69 MPa. Key: 1, screw-top brass container; 2, starch membrane; 3, Viton O-rings; 4, brass ring.

The solutions were quickly absorbed into the MCF matrix. The solvent was removed from the MCF by drying in nitrogen until no further decrease in weight was observed.

Headspace Analysis. Wheat starch or high-amylose corn starch MCF sheets prepared previously were cut into pieces (~4.5 cm²) weighing 0.5 g. The starch foam pieces were placed in glass jars (130 mL) with lids containing a Teflon membrane and septum through which headspace samples could be drawn. Experiments were performed at 22 °C. A sample (5.0 μL) of test compound was deposited directly on the surface of the MCF sample before the lid of the jar was tightly closed. For comparison, an identical jar containing 0.5 g of wheat starch or HACS powder in place of the wheat starch or HACS MCF was prepared. After the test compound was deposited directly on the starch powder, the jars were sealed with the lid and agitated for 5 s to achieve uniform distribution. All samples were compared to a control consisting of a sealed, empty glass jar into which was deposited 5.0 μL of test compound.

The jars were allowed to equilibrate for 30 min at room temperature (22 °C) before a headspace sample (1.0 mL) was drawn with a gastight glass syringe. The sample was immediately injected into a gas chromatograph (GC) (Hewlett-Packard, model 5890) equipped with a flame ionization detector and a fused silica capillary column (60 m × 0.32 mm i.d.) coated with DB-1. The GC oven temperature was optimized for each compound but was kept constant for a given sample. Second and third samples were drawn from each jar at 30-min intervals.

Compressed MCF. A starch plastic was made by compressing wheat starch MCF sheets as previously described (13). The starch MCF was first equilibrated for at least 48 h in a humidity chamber (50% relative humidity) and then cut into disks (5 cm diameter). A hydraulic press was used to compress the MCF disks at three different pressures (1.4, 6.9, and 69 MPa) to make the plastic with thicknesses of 0.33, 0.17, and 0.10 cm, respectively. Pressed and uncompressed disks of MCF were ground to size (3.8 cm).

Vapor Transmission Rates. Diffusion cells were made of screw-top brass containers with a brass ring that could be screwed securely in place (see Figure 1). The ring and the container each had a lip about 3 mm wide; the lips were aligned when the ring was mounted. The disks (3.8 cm) of uncompressed and compressed MCF were assembled in the diffusion cells between the ring and the container. The disks were sealed in place with O-rings made of Viton (DuPont Dow, Wilmington, DE). Preliminary tests were performed to verify that the sealed containers had airtight seals. The test consisted of sealing a needle in the sidewall of the sealed diffusion cell. An increase in air pressure within the cells was created using a 200-mm column of water. The test was considered successful when no significant drop in pressure occurred within a 2-min test period.

The assembled diffusion cells containing the test compound were placed in a chamber containing a desiccant (CaSO₄) to maintain a constant low humidity and a fan to minimize boundary effects at the surface of the diffusion cells. The weight loss for each diffusion cell was recorded each day at the same hour. The only exception was for diffusion cells containing acetone that were weighed at 4-h intervals. The vapor transmission rate (VTR) was calculated as follows:

$$VTR = GT/tA$$

where G is the weight change (grams), T is the thickness of the starch membrane (meters), t is the time (hours), and A is the area of the starch membrane (square meters).

Scanning Electron Microscopy. Samples of MCF were prepared as intact specimens to observe the foam surface, or they were fractured to expose the interior structure. The wheat starch samples were mounted onto a stub using a resin/colloidal graphite mixture and sputter-coated for 45 s with gold/palladium. The HACs samples were mounted onto a stub using conductive tape and sputter-coated for 90 s with gold/palladium. All samples were viewed at 3 kV in a Hitachi (model S4700) scanning electron microscope.

Experimental. Each experiment was conducted using three replicates for each treatment. Differences among means were determined by analysis of variance. All statistical analyses were performed using standard methods (SigmaStat, SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Microcellular Foam. The MCF beads made of HACs were approximately one-half the density of wheat starch MCF sheets (0.12 vs 0.26 g/cm³, respectively). The sheets of wheat starch MCF were approximately 4.3 mm thick. The thicknesses of wheat starch MCFs compressed using 1.4, 6.9, and 69 MPa force averaged 3.3, 1.8, and 1.0 mm, respectively. Micrographs (SEM) showed that uncompressed MCF microstructure consisted of amylose strands that formed a porous network with pore sizes generally smaller than 2 μ m (Figure 2). Micrographs (SEM) of the HACs MCF surface indicated that the surface was similar in appearance and porosity to the interior portion of the MCF (Figure 2A,B). In contrast, the surface of the wheat starch MCF was somewhat less porous than the interior portion (Figure 2C,D). The difference may be due to a slight compression at the surface of the MCF during the drying step. The wheat starch MCF was equilibrated in ethanol and then air-dried, in contrast to HACs MCF that was equilibrated in ethanol followed by liquid carbon dioxide and then dried at the critical point, a process that virtually eliminated surface tension. Small amounts of water present in the last ethanol dehydration step used to displace water in the wheat starch gel could have accumulated at the gel surface while drying and created sufficient surface tension to compress the surface microstructure.

The porosity of the surface and interior of the compressed wheat starch MCF appeared to decrease with incremental increases in compression force (Figure 2C–J). The MCF compressed at 69 MPa contained regions that were transparent, indicating that the pores, cavities, or other imperfections that scatter light were nearly eliminated. However, other regions of the sample were opaque and contained small pores (Figure 2I,J). The interior of the starch plastics was difficult to observe in its unaltered state because the samples were fractured to expose the interior. The fracture process most likely created cracks and cavities that were not present in intact samples. Nevertheless, the micrographs show that the interior of the starch plastics became more compacted as the compression force applied was increased.

Headspace Analysis. Lowering the vapor pressure of volatile compounds is important in effectively reducing the rate at which they are released into the environment (3). A quantity of test compound that was within its sorptive capacity (1% w/w) was added directly to the MCF before samples were drawn for headspace analysis. Table 1 lists the ratios of the headspace partial pressure (p) in sealed jars containing starch powder or MCF loaded with test compound to that of jars containing only the test compound (p°). The starch powders typically lowered the partial pressure compared to the partial pressure of a

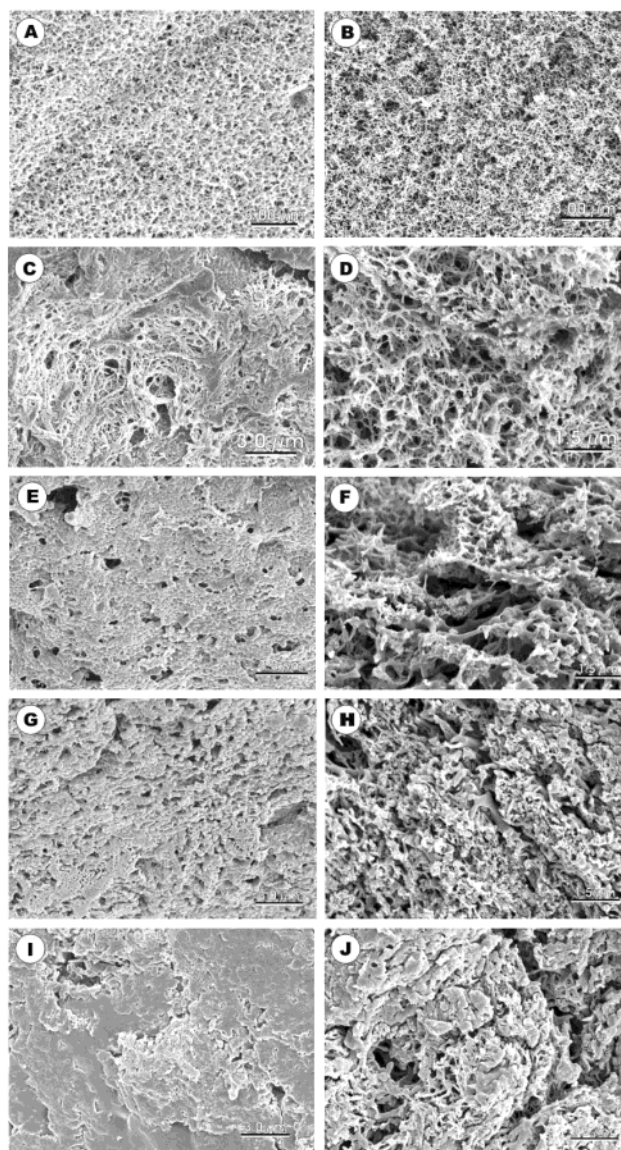


Figure 2. Scanning electron micrographs of high-amylose corn starch (A,B) and wheat starch (C–J) microcellular foams (MCFs). The surface (A,C,E,G,I) of the MCF typically was less porous than the matrix (B,D,F,H,J), especially in samples compressed at 1.4 (E,F), 6.9 (G,H), and 69 MPa (I,J). Scale bar for A,C,E,G,I = 3 μ m; scale bar for B,D,F,H,J = 1.5 μ m.

reference jar. The exception was HACs powder that had values similar to the reference ($p/p^\circ \approx 1$). The ratio of partial pressures was typically lower for wheat starch powder compared to HACs powder with the exception of 3-methyl-2-cyclohexen-1-one (Table 1). The MCF samples all had significantly lower ratios than the starch powder samples.

There was no increase in sorption (lower p/p°) in MCF loaded with either PA or SO, even though the test compounds were quite nonpolar. In fact, the p/p° for (*S*)-(–)-limonene was slightly higher for MCF containing SO compared to the MCF sample without SO. The reason the PA and SO were ineffective in lowering the p/p° may have been their poor distribution within the MCF. The PA and SO may have simply saturated the pores in a region of the MCF rather than forming a thin coating on the fibrous matrix that would have exposed much more surface area and allowed greater sorption to occur.

The HACs MCF had significantly lower p/p° values for (*S*)-(–)-limonene, 3-pentanone, and 9-decen-1-ol than the wheat

Table 1. Ratio of Partial Pressure (p) of Compounds in Headspace of Jar with Wheat Starch (WS) or High-Amylose Corn Starch (HACS) Powders or MCF to That (p^0) in Reference Flask with No Starch (Equal to Corresponding GC Peak Area Ratio)

compound ^a	p/p^0 ^b					
	HACS powder	WS powder	WS MCF	WS MCFPA	WS MCFCS	HACS MCF
(S)-(-)-limonene	1.08 a	0.870 b	0.201 d	0.269 cd	0.365 c	0.137 d
3-pentanone	0.834 a	0.547 b	0.112 c	0.091 c	0.136 c	0.069 d
3,5-lutidine	0.831 a	0.547 b	0.112 c	0.091 c	0.136 c	0.099 c
3-methyl-2-cyclohexen-1-one	0.650 a	0.793 a	0.294 b	0.202 b	0.210 b	0.271 b
9-decen-1-ol	0.271 a	0.248 a	0.040 b	0.056 b	0.050 b	0.0037 c
(E)-5-decen-1-yl acetate	0.332 a	0.210 b	0.066 c	0.070 c	0.081 c	0.044 c
(E)-2,4-decadienoate	0.345 a	0.197 b	0.071 c	0.067 c	0.063 c	0.020 c

^a Compounds were added in amounts of 5.0 μ L to an empty 130-mL jar sealed with a Teflon membrane or a jar containing 0.50 g of starch powder, MCF, or MCF containing palmitic acid (PA) or silicon oil (SO). ^b Values within rows followed by a different letter are significantly different ($p < 0.05$).

Table 2. Vapor Transmission Rate (VTR) of Microcellular Wheat Starch (MCF) and Wheat Starch Plastics (SP) Formed at Three Compression Forces (1.4, 6.9, and 69 MPa)

compound ^a	vapor pressure at 25 °C (mm)	VTR (g/h·m) ^b			
		MCF	SP		
			1.4 MPa	6.9 MPa	69 MPa
(S)-(-)-limonene	4	0.091	0.062	0.041	0.0028
3-pentanone	28	1.6	1.2	0.47	0.035
3,5-lutidine	3.0	0.065	0.053	0.019	0.0023
3-methyl-2-cyclohexen-1-one	4.2	0.076	0.047	0.028	0.0098
9-decen-1-ol	0.2	0.036	0.035	0.019	0.0072
(E)-5-decen-1-yl acetate	0.020	0.021	0.013	0.012	0.0048
(E)-2,4-decadienoate	0.04	0.025	0.018	0.013	0.0042
ethanol	50	1.4	1.0	0.37	0.022
acetone	375	7.8	5.5	1.9	0.03
water	20	0.62	0.46	0.16	0.05

^a Starch sample was sealed in a diffusion cell and served as a membrane through which vapor of each compound passed. ^b The VTR values represent amount (grams) of vapor per unit of time (hours) passing through a sample of unit thickness (meters) and surface area (square meters).

starch MCF, even though the HACS powder samples generally had higher partial pressure ratios than the wheat starch powder samples (**Table 1**). The reason for the lower partial pressure ratios for the HACS MCF may be its composition and microstructure. The HACS has a higher percentage of amylose that comprises the porous, fibrous component of the MCF matrix (6, 7). The amylose portion of gelatinized starch has been shown to form complexes with a wide array of molecules, while ungelatinized starch is relatively inert (14). It may be that the amylose fraction in MCF is able to form complexes with volatiles even though the MCF has very low water content. The amylopectin portion of starch shows little tendency to form complexes (14). This could explain why HACS generally had better sorptive properties than wheat starch MCF (with a higher amylopectin content), and it explains why the ungelatinized starch powders were relatively inert.

The microstructure of the MCF is perhaps more responsible for the sorptive properties observed than any other factor. This was made evident in studies where water was added to the MCF, which effectively disrupted the microstructure and resulted in the release of much of the sorbed compound (8). Further work showed that starch foams containing relatively large cells were ineffective in sorbing volatile compounds (8). MCF has a porous, fibrous matrix composed of amylose with a significant percentage of pores in the range of 5–14 Å. MCF also contains a dense, nonporous amylopectin fraction localized primarily in the remnants of the starch granules that are interspersed throughout the MCF matrix (6). HACS MCF has roughly twice the amylose content and half the density compared to the wheat

starch MCF. The higher porosity in HACS MCF could expose more surface area and provide a greater number of small pores, resulting in increased sorption of volatile compounds.

Rates (VTR) of Starch Plastic. A coating on the MCF may be necessary in the case where the vapor pressure of a volatile compound needs to be lowered beyond that obtainable with MCF alone. Carbohydrate coatings are commonly used in foods to control release rates and reduce evaporation of volatile compounds (3). These coatings could be effectively used to coat MCF except that they are normally applied as an aqueous solution that could cause the porous microstructure of the MCF to collapse from surface tension during the drying step. An alternative coating technique is to encapsulate the MCF between layers of compressed MCF, which has properties similar to those of some plastics, depending on the compressive force used (13).

The VTR was measured to assess the effect of compression on the permeability of MCFs to various volatile compounds including ethanol, acetone, and water. The VTR was inversely related to the compression force used in making a starch plastic (**Table 2**). The VTRs for all compounds tested in MCFs compressed at 1.4, 6.9, and 69 MPa were 28, 62, and 91%, respectively, lower than the VTR values of uncompressed MCF samples. The results demonstrate that compressing the MCFs with variable amounts of force can make a starch barrier with variable permeability.

The vapor pressure and chemical properties of a given volatile compound are also factors that may affect VTR. Bangs and Reineccius (15) showed in spray-dried samples that retention of volatile compounds was related to the relative volatility of

the compounds. Accordingly, the VTR values (**Table 2**) tended to be higher for test compounds with higher vapor pressures, especially for the uncompressed MCFs and MCFs compressed using 1.4 and 6.9 MPa force (**Table 2**).

The data for MCF compressed with 69 MPa force indicated that the VTR was affected less by vapor pressure but more by chemical properties than the other samples tested. Goubet et al. (3) reported that retention of volatile compounds encapsulated in carbohydrate coatings was highest in alcohols, followed by ketones and esters and finally acids. The highest VTR in the 69 MPa sample was for water, which has a high affinity for starch and acts as a plasticizer. The high number of hydroxyl groups in starch contributes to hydrogen bonding and water absorption (16). It explains why starch preferentially absorbs water when water–solvent mixtures are exposed to dry starch (17). The VTR for ethanol was nearly equal to that of acetone (**Table 2**), further indicating that vapor pressure contributed less to the VTR in the 69 MPa sample relative to other samples tested. Other properties that can affect the diffusion rate of a compound include polarity, molecular weight, and steric hindrance (3). These properties likely become more important relative to vapor pressure as compression of the MCF is increased.

The results of this study indicate that MCF has physical properties that make it potentially useful as a slow-release agent for volatile agricultural chemicals. The MCF matrix is able to quickly absorb liquids and lower the vapor pressures of different compounds by vapor sorption. The release rate of volatiles can be further lowered by encapsulating the MCF in a compressed MCF coating to achieve a desired VTR. Encapsulation could be accomplished by placing a MCF loaded with compound into a cavity formed in several layers of compressed MCF. The entire assembly could then be pressed together to form a seal. It may also be possible to lightly mist the surface of a MCF loaded with compound with an aqueous solution, followed by air-drying to allow surface tension to compress the outer region of the MCF and seal the surface of the MCF.

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