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Permeability of Starch Gel Matrices and Select Films to Solvent Vapors

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Volatile agrochemicals such as 2-heptanone have potential in safely and effectively controlling important agricultural pests provided that they are properly delivered. The present study reports the permeability of starch gel matrices and various coatings, some of which are agricultural-based, that could be used in controlled release devices. Low-density, microcellular starch foam was made from wheat, Dent corn, and high amylose corn starches. The foam density ranged from 0.14 to 0.34 g/cm^3, the pore volume ranged from 74 to 89%, and the loading capacity ranged from 2.3 to 7.2 times the foam weight. The compressive properties of the foam were not markedly affected by saturating the pore volume with silicone oil. The vapor transmission rate (VTR) and vapor permeability (VP) were measured in dry, porous starch foam and silicone-saturated starch gels. VTR values were highest in foam samples containing solvents with high vapor pressures. Silicone oil-saturated gels had lower VTR and VP values as compared to the dry foam. However, the silicone oil gel did not markedly reduce the VP for 2-heptanone and an additional vapor barrier or coating was needed to adequately reduce the evaporation rate. The VP of films of beeswax, paraffin, ethylene vinyl alcohol, a fruit film, and a laminate comprised of beeswax and fruit film was measured. The fruit film had a relatively high VP for polar solvents and a very low VP for nonpolar solvents. The laminate film provided a low VP for polar and nonpolar solvents. Perforating the fruit film portion of the laminate provided a method of attaining the target flux rate of 2-heptanone. The results demonstrate that the vapor flux rate of biologically active solvents can be controlled using agricultural materials.

KEYWORDS: Starch; microcellular foam; 2-heptanone; *Apis mellifera* L.; *Varroa destructor*

INTRODUCTION

The controlled release of volatile agrochemicals is of growing interest in pest management strategies. As much as 90% of applied conventional agrochemicals is wasted because of both inefficient application methods and unfavorable weather conditions (*1*). The advantages of controlled release delivery are that the active ingredient is delivered at a more uniform rate, "over" and "under" dosing is minimized, human exposure is minimized, less active ingredients are required, the control period is extended, and beneficial organisms are less impacted (*1*–*3*). Many different types of controlled release systems have been developed for agricultural applications including hollow fiber membranes, capillaries, and polymer devices that swell and absorb the active agent (*4*–*7*). Atterholt et al. (*8*) encapsulated

the sex pheromone of Oriental Fruit moth in a paraffin emulsion preparation and demonstrated a constant release rate over a period of more than 100 days.

A potentially important controlled release application is in the honeybee industry. Honeybees, *Apis mellifera* L., produce more than $270 million worth of honey and pollinate over $14 billion worth of crops annually in the United States alone (*7*). A serious worldwide threat to honeybees is the parasitic mite, *Varroa destructor* (*7*, *9*–*11*). Varroa mites can deform developing bees, cause weight loss and premature death, and transmit various viral diseases (*7*, *9*, *12*, *13*). Mite infestations can completely destroy infected honeybee colonies in as little as a few weeks when remedial measures are not taken (*9*, *14*).

Methods of controlling *Varroa* include biotechnical, genetic, and chemical means (*10*). Biotechnical measures such as mite trapping devices, while effective, are labor intensive and not particularly efficient (*10*). A promising long-term approach is the development of new bee lines using resistant honey bees

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and the use of entopathenogenic fungi (*10, 15*). Chemical control of *Varroa* with pyrethroids and organophosphates has proven effective in the past, but several mite populations have developed a chemical resistance and are now more difficult to control. An additional problem with chemical control is that pesticide residues have been detected in both the wax and the honey harvested from treated colonies (*16, 17*). In past years, pesticide contamination was primarily a concern only for honey production, but today, the concern is also for beeswax contamination since beeswax is now used in cosmetics and pharmaceutical products (*17*). Other chemicals have been evaluated as potential acaricides for controlling *Varroa* but have many of the same limitations.

Recently, there has been interest in the acaricidal effects of 2-heptanone. 2-Heptanone is a pheromone produced by adult worker honeybees. It is a volatile liquid produced in the mandibular gland that solubilizes beeswax and is used to manufacture beeswax comb and propolis and to solubilize plant resins (*7, 18, 19*). 2-Heptanone is found in beeswax at low concentrations and is considered a natural component of beeswax. 2-Heptanone vapor acts as an attractant for *Varroa* mites at low concentrations but has acaricidal properties at higher concentrations (*7*).

Starch has been explored in slow release systems for agrochemicals because of its degradability in many agricultural environments and versatility in processing. Carr et al. (*20*) used an extrusion process to encapsulate an active herbicide in a starch extrudate. Wing et al. (*21*) used jet cooking to disburse an herbicide in a cornstarch melt that was dried and finally ground to the desired particle size. The amount of herbicide encapsulated in the starch ranged from 36 to 58% depending on processing parameters selected. In yet another approach, McGuire et al. (*22*) controlled the release of an herbicide by chemically linking the active ingredient to pregelatinized starch. The active ingredient was released as the starch component degraded in the field.

Glenn and Irving (*23*) described a process for making a food-grade starch-based microcellular foam. The foam was composed of an open matrix of pores generally smaller than 2 μm with some pores in the range of 5−14 Å. The small pores and large collective pore volume of the starch microcellular foam enable the foam to absorb several times its weight of a given solvent (*24*). The foam could be made into sheets of varying thicknesses or beads of varying diameters (*25*). Starch microcellular foam could be useful in reservoir type dispensing systems to control the release of various volatile agrochemicals. It has the advantage of being easily degraded and, unlike many of the other current dispensing systems, would not need to be recovered from the field when the agrochemical reserves were spent.

The objective of this study was to investigate the physical and mechanical properties of solvent-filled starch microcellular foam and determine the vapor transmission rate (VTR) and vapor permeability (VP) of dry starch foam, starch−solvent gel (SSG) matrices, and films made of waxes and/or a fruit components. Particular emphasis was directed toward 2-heptanone due to its importance in apiculture.

MATERIALS AND METHODS

Materials. Unmodified wheat starch (Midsol 50) was purchased from the MGP Ingredients, Inc. (Topeka, KS), and Dent cornstarch (Melojel) and high amylose corn starch (HACS) (Hylon VII) were purchased from the National Starch and Chemical Co. (Bridgewater, NJ). Silicone oil (CAS registry no. 63148-62-9), 2-heptanone (CAS registry no. 110-43-0), acetone, and glacial acetic acid were purchased from the Sigma-Aldrich Co. (St. Louis, MO). Microcrystalline wax, paraffin, and beeswax were acquired from Protex Wax (Oakland, CA). Poly(ethylene-vinyl alcohol) copolymer resin film (E 105, 48 mol % ethylene, 15 μm thickness) was provided by EVAL Company of America (Houston, TX). Peach fruit film (100 μm thick) processed from a 3:1 blend of peach puree:pectin (BioTech Films, Tampa, FL) was used for fruit film tests.

SSG Preparation. SSGs of wheat and Dent corn starches were prepared by heating a 10% (w/w) aqueous starch slurry to 90 °C and maintaining the temperature for 10 min with constant stirring. The starch melt was poured into a mold (30 cm × 40 cm × 0.7 cm), covered with aluminum foil, and kept in a refrigerator overnight. The HACS sample was made by heating a 10% (w/w) aqueous starch slurry to 140 °C and maintaining that temperature for 10 min using a pressure reactor (Parr Instrument Co., Moline, IL). The melt was cooled to 70 °C and poured into a mold, covered, and refrigerated as previously described. The chilled starch samples were transferred from the molds to a pan containing 40% ethanol (w/w). Sufficient ethanol was added to the pan to completely submerge the starch sample. The samples were dehydrated by exchanging the ethanol with increasingly higher concentrations (40, 70, and 90% and three changes of 100% ethanol) to make an ethanol-saturated SSG.

Silicone oil-saturated SSG samples were made from ethanol-saturated SSG by first cutting cylindrical pieces (ca. 2 cm dia., 0.7 cm thickness) using a boring tool. The ethanol-saturated SSG pieces were equilibrated in a 1:1 mixture of ethanol and silicone oil followed by equilibration in 100% silicone oil for 24 h each. 2-Heptanone-saturated SSG samples were made from ethanol-saturated SSG cylindrical pieces by equilibration for at least 12 h each in four changes of 10 volumes of 2-heptanone. SSG samples containing a 1:1 mixture of 2-heptanone and silicone oil were made by equilibrating ethanol-saturated SSG cylindrical pieces for 12 h in 10 volumes of a 1:0.5:0.5 mixture of ethanol:silicone oil: 2-heptanone mixture followed by equilibration in four changes of 10 volumes of a 1:1 silicone oil:2-heptanone mixture. A similar exchange procedure was used to make SSGs containing 4:0, 3:1, 1:3, and 0:4 2-heptanone:silicone oil blends.

Dry Foam Preparation. Dry foam samples were made from aqueous gels of wheat and Dent corn starches by first equilibrating the gels in a graded ethanol series as previously described. The gels shrank and hardened during the ethanol dehydration process and developed sufficient compressive strength to be air-dried without collapsing from surface tension. The HACS sample, however, completely collapsed when air-dried. To prevent the foam structure from collapsing during the drying process, surface tension forces were minimized for the HACS gel by first equilibrating it in an ethanol series as previously described. The samples were then equilibrated in CO_2(l) and critical point dried (Autosamdri-815 critical point dryer, Tousimis Research Corp., Rockville, MD) producing a dry foam product.

Scanning Electron Microscopy. Dry starch foam samples were cryofractured in ethanol as per Humphreys et al. (*26*). Briefly, foam samples were cut into rectangular cubes of approximately 5 mm on the longest side using a sharp razor blade. The cubes were soaked in two exchanges of 100% ethanol for 1 h. The samples were removed from ethanol using a tweezers and dropped immediately into liquid nitrogen and fractured with a razor blade held in a clamp. The razor blade and clamp were equilibrated to liquid nitrogen temperatures prior to the fracture. The pieces were then collected using a liquid nitrogen-chilled tweezers and dropped back into ethanol. Cryofractured pieces were critical point dried and mounted onto aluminum specimen stubs using double adhesive-coated carbon tabs (Ted Pella, Inc, Redding, CA), viewed, and photographed in a Hitachi S4700 field emission scanning electron microscope (Hitachi, Japan).

Physical and Mechanical Properties. The density of samples was calculated from measurements of sample weight, thickness, and diameter. The cumulative pore volume (V_p) was calculated as follows:

$$V_p = [V_t - V_s] \times 100$$

where V_t = total volume of foam and V_s = foam dry wt/specific gravity for starch (1.3 g/cc). The compressive properties of the samples were tested as per ASTM D1621 (*28*). Briefly, cylinders of dry starch foam and silicone oil-filled gels of wheat, corn, and HACS were deformed

Starch Gel Matrices

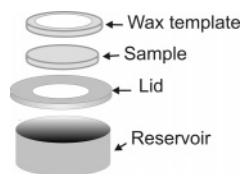*J. Agric. Food Chem.,* Vol. 54, No. 9, 2006 **3299**

Figure 1. Diffusion cell assembly used to measure VTRs. All components were assembled in the order illustrated. The edges of the lid and sample were sealed with a wax mixture to prevent vapor leaks.

Table 1. Density, Pore Volume, Oil:Starch Ratio, Compressive Strength, and Modulus of Corn, Wheat, and HACS Foam and Silicone Oil-Saturated Gels

	corn	corn/SO	wheat	wheat/SO	HACS	HACS/SO
density (g/cm^3)	0.34 c^a	1.1 a	0.27 c	1.1 a	0.14 b	1.1 a
pore volume (%)	74 a		79 a		89 b	
oil/starch (w/w)		2.3 a		3.1 a		7.2 b
strength (MPa)	1.4 c	2.0 e	0.98 b	1.0 b	0.096 a	0.17 d
modulus (MPa)	23 c	36 d	11 b	20 c	2.3 a	2.3 a

^{a} Differences in values within rows followed by a different letter are significant (0.05 level).

under compression to 10% of the sample thickness using a universal testing machine (model 5500R, Instron Corp., Canton, MA). Compression tests were performed at a constant crosshead speed (2.54 mm/min). The compressive strength at 10% deformation was recorded.

Vapor Transmission and Permeability Tests. The VTR was tested and measured based on ASTM methods (*27*). Tests were performed using diffusion cells (**Figure 1**) made of aluminum specimen dishes with lids containing a hole (1.27 cm). The sample was centered over the hole and sealed in place with a wax template with a hole matching that of the lid (1.27 cm). The wax was comprised of a 3:2 mixture of paraffin and microcrystalline waxes as per ASTM methods (*27*). Tests were conducted by first pipetting 10 g of solvent into the reservoir. The diffusion cells were assembled as per **Figure 1** and made vapor tight by sealing the edges of the sample to the lid and sealing the edge of the lid with the wax mixture. The diffusion cells were placed in a poly(methyl methacrylate) cabinet equipped with a ventilation fan. The airflow velocity was 9.8 m/s, and the airflow volume was 4.7 volume changes per second (9.9 m^3/min). All tests were performed at room temperature.

The VTR was calculated as follows:

$$\text{VTR} = G \cdot d/t \cdot A$$

where G = weight change (g), t = time (s), d = sample thickness (m), and A = area of starch cylinder (m^2). The VP was calculated from the VTR, and the vapor pressure difference (Δp) between the two sides of the samples where VP equals VTR/Δp.

VTR and VP data were recorded for the dry foam and silicone oil-saturated SSG. Two controls were tested that consisted of a diffusion cell with an open orifice (no sample sealed to the lid) and a diffusion cell with an aluminum disk sealed over the hole. The liquids tested included water, ethanol, acetone, 2-heptanone, dichloromethane, and acetic acid.

VP data were collected for wax films (1.5 mm) made of beeswax, paraffin wax, or a 1:1 mixture of paraffin and beeswaxes. VP data were also collected for ethylene vinyl alcohol (EVOH) film, fruit film, and a laminate film (1 mm) consisting of beeswax (0.9 mm) and fruit film (0.10 mm). The films were sealed to the outer surface of diffusion lids with wax after which the diffusion cells were assembled and sealed as described earlier.

Laminate films of beeswax and fruit film with a range in flux rates were prepared using perforated fruit film. This was done by perforating the fruit film with a small boring tool (1 mm diameter) and then pouring a layer (0.7 mm) of molten wax over the film and cooling in air. The laminate samples were mounted on the diffusion cell as previously described. The flux rate of the 2-heptanone and the cumulative perforated area for each sample were recorded.

Evaporation Rates. The rate of 2-heptanone vapor release was determined gravimetrically for samples of starch gels loaded with 2-heptanone. HACS was used in the tests since the HACS had higher loading levels than gels made of either the wheat or the corn starches. Various mixtures of 2-heptanone and silicone oil were prepared with a range of 2-heptanone:silicone oil ratios (4:0, 3:1, 1:3, and 0:4) using a solvent exchange procedure similar to that previously described. HACS SSG samples were prepared from each of the mixtures and then placed in a poly(methyl methacrylate) cabinet equipped with a ventilation fan as described earlier. There was no significant weight loss over time in samples containing only silicone oil. Therefore, cumulative weight loss observed in each sample over time was attributed solely to evaporation of 2-heptanone. The total amount of 2-heptanone

loaded in each sample was verified by recording the difference in the initial and final sample weight. The cumulative weight loss (%) over time was determined by dividing the cumulative weight loss by the total amount of 2-heptanone loaded in the sample.

The effect of various films on the evaporation rate of 2-heptanone was studied using the HACS cylindrical pieces described earlier, which were saturated with a mixture of 2-heptanone:silicone oil (1:1). The 2-heptanone:silicone oil mixture was used because beeswax is soluble in 2-heptanone and is more stable in a mixture of 2-heptanone and silicone oil. Containers filled with either beeswax, paraffin, or a 1:1 blend (beeswax:paraffin) were placed in an oven (80 °C) to melt the waxes. A wax layer was formed on the HACS cylindrical pieces by dipping them in the molten wax and cooling them in air. Multiple applications were necessary to entirely seal the gel in wax due to difficulty in getting the molten wax to adhere to the gel substrate. The wax coating was ultimately continuous and completely enveloped the samples, but the thickness of the coating was not uniform. Other HACS gels were coated with a laminate of beeswax and fruit film. The coating was applied by first cutting the fruit film to size and carefully folding it to completely envelope the sample. The sample was dipped into molten beeswax that easily adhered to the film surface and formed a continuous film encompassing the outer surface of the sample. The cumulative weight loss (%) over time was recorded.

Experimental. A completely randomized design was used for VTR and VP experiments. All experiments were performed in triplicate except for the textural tests (five samples) and density readings (10 samples). All statistical analyses were performed using standard methods (SigmaStat, SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Physical Properties of Starch Gels. All of the dry starch foam samples were white and opaque. As mentioned earlier, the wheat and Dent corn starch samples shrank considerably during the ethanol dehydration step. This densification process provided the gels sufficient strength that they could be simply dried in air. Earlier results showed that the density of foam made of wheat or Dent corn starch was not markedly lowered by the critical point drying process (*23*). However, foam made of HACS had less compressive strength and collapsed into a dense mass when simply air-dried and, therefore, needed to be critical point dried to preserve the foam structure. The wheat and Dent corn starch foam samples had a similar density whereas the HACS foam was much lower in density (**Table 1**).

The scanning electron micrographs of the cryofractured surfaces of dry starch foams revealed that the starch matrix was composed of a fibrous, open cell structure with very small pores (**Figure 2**). The wheat and the corn starch samples each had remnants of starch granules interspersed throughout the foam matrix (**Figure 2a−d**). The HACS foam had relatively few starch granule remnants and a smaller pore size as compared to the wheat and corn samples (**Figure 2e−g**). This, coupled with the lower density of the HACS, may account for the lower compressive strength and the need for the samples to be critical point dried to keep them from collapsing from surface tension
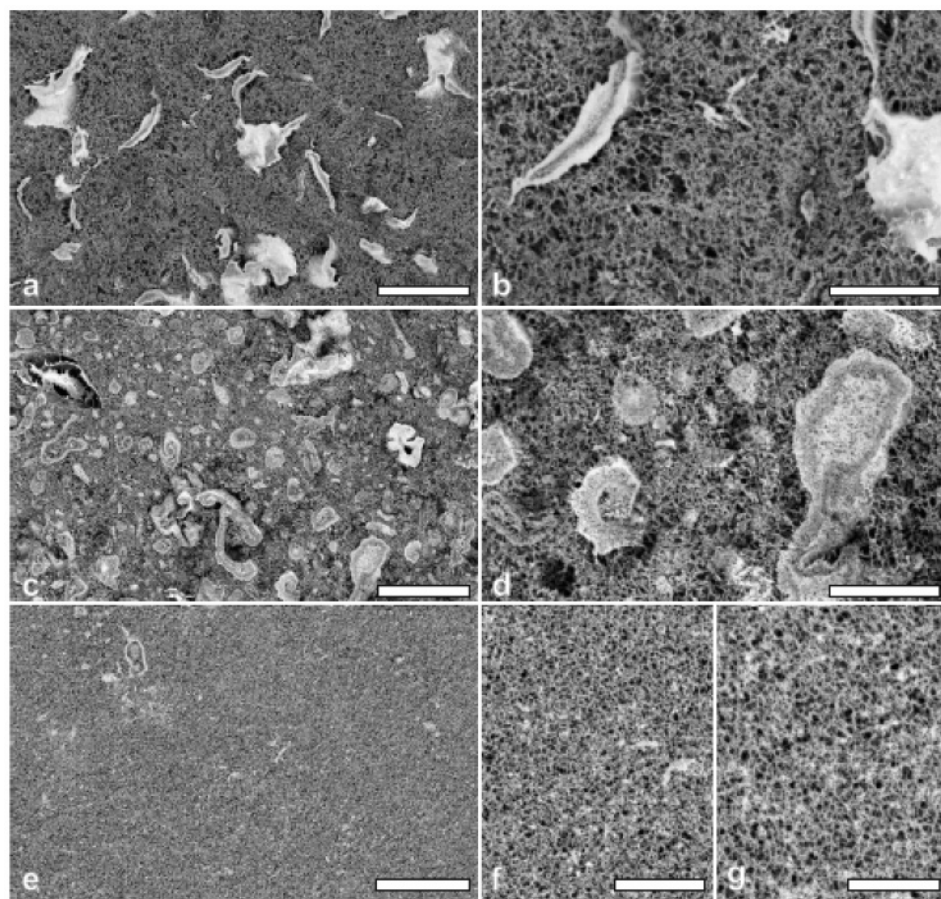
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Figure 2. Scanning electron micrographs of cryofractured surfaces of dry starch foam samples from wheat (**a**,**b**), Dent corn (**c**,**d**), and HACS (**e**–**g**). Note the starch granule remnants interspersed throughout the starch matrix. The scale bar for **a**, **c**, and **e** represents 25 μm. The scale bar for **b**, **d**, and **f** represents 10 μm. The scale bar for **g** represents 4 μm.

forces. The extremely small pore size and the large cumulative pore volume (**Table 1**) of the foam contribute to the ability of the samples to absorb and hold by capillary force a large volume of liquid.

Starch gel matrices can be useful as a reservoir for controlled release systems provided that the starch matrix remains stable in the presence of the test liquid. In the case of aqueous solutions, preliminary tests indicate that the starch matrix loses strength when aqueous solutions are absorbed into dry foam samples. Nonpolar liquids with very low vapor pressures such as silicone oil can be absorbed into the starch matrix without deteriorating mechanical properties (**Table 1**). Starch gel matrices from different sources effectively held several times their weight in silicone oil (**Table 1**). The oil-filled gels of wheat and Dent corn starch were white and opaque whereas the oil-filled HACS gel was transparent. The oil-filled gels were easily handled and did not expel oil unless forcibly compressed. There was no significant difference measured in the density of silicone oil-filled samples among the three starches tested. The HACS sample was unique in that it absorbed more than twice the amount of silicone oil than the Dent corn or wheat starch foam samples on a weight basis.

The microporous structure of the starch matrix was effective in containing the silicone oil such that the gel could be readily handled without regard to leakage. However, when the gels were placed under compression stress, the oil was slowly expelled to relieve the stress. This is somewhat expected since the dry, air-filled foams are compressible and have an open cell structure. The dry, air-filled starch foam samples do not fracture under compressive stress but simply densify to form a plastic-like material as has previously been described (*29*). In contrast, oil-filled gels eventually fractured when deformed greater than 10% (data not shown). The most likely cause of the failure was due to the inability of the gels to expel oil quickly enough to dissipate the mounting compressive stress. Despite the eventual failure of starch gels subjected to increasing compressive stress, the results indicate that starch gel matrices can effectively contain nonaqueous liquids while maintaining mechanical strength. These properties make starch gels particularly suitable as a reservoir material for controlled release devices because they effectively prevent leakage of solvent.

Vapor Transmission and Permeability. Controlling the vapor flux rate of a biologically active solvent or liquid is important in effective controlled release devices. One way to control the vapor flux rate of a liquid is to choose a matrix material that is able to lower the vapor flux of volatile compounds to a desirable range. Vapor transmission through the starch foam matrix was investigated to determine the VTR and VP of the foam for a host of solvents with different vapor pressures and chemical properties that could be of interest for different controlled release applications.

It is well-known in the flavor industry that starch films and coatings are very good barriers to oxygen and many volatile flavor compounds. The food industry typically uses carbohydrates including chemically modified starches with emulsifying properties or dextrans to commercially encapsulate volatile flavor compounds using spray drying or extrusion processes (*30*). In spray drying, an emulsion is formed in which the volatile

Starch Gel Matrices

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Table 2. VTR of Starch Foam and Starch/Silicone Oil Gels to Various Solvent Vapors[a]

	water	ethanol	acetone	hexanes	dichloromethane	2-heptanone	acetic acid
VP (kPa) at 25 °C	3.17	7.87	30.8	20.2	58.2	0.48	2.07
control open	78 (13)[b]	490 (13)	2250 (26)	1830 (15)	6700 (220)	97 (5.6)	270 (12)
closed control	0.0030 (0.0019)	0.022 (0.015)	0.017 (0.022)	0.033 (0.030)	0.18 (0.058)	0.036 (0.0058)	0.00058 (0.00030)
Dent corn—dry foam	37 (0.53)	230 (4.8)	1170 (210)	790 (24)	3141 (182)	28 (1.1)	61 (2.1)
wheat—dry foam	50 (7.8)	330 (12)	1800 (290)	1170 (44)	6090 (260)	33 (2.8)	83 (3.6)
HACS—dry foam	35 (3.0)	375 (26)	2180 (150)	1820 (120)	5950 (96)	36 (4.7)	86 (4.2)
corn/SO	1.4 (0.67)	4.7 (0.92)	110 (16)	140 (15)	340 (19)	13 (2.8)	5.3 (0.70)
wheat/SO	0.53 (0.73)	8.3 (1.3)	180 (10)	232 (8.6)	500 (56)	18 (2.0)	11 (0.31)
HACS/SO	0.86 (0.83)	10 (1.3)	260 (19)	322 (19)	760 (130)	29 (5.8)	11 (0.97)

[a] The VTR values ($\times 10^{-6}$ g m/s m^2) represent the amount (g) of vapor per unit of time (h) passing through a sample of unit thickness and unit surface area (m^2). [b] Values in parentheses indicate standard deviation.

Table 3. VP of Starch Foam and Starch/Silicone Oil Gels to Vapors of Select Liquids[a]

	water	ethanol	acetone	hexanes	dichloromethane	2-heptanone	acetic acid
closed control	0.0096 (0.0059)[b]	0.028 (0.019)	0.0054 (0.0070)	0.017 (0.015)	0.030 (0.010)	0.75 (0.12)	0.0028 (0.0015)
Dent corn—dry foam	120 (1.6)	290 (6.1)	380 (69)	390 (12)	540 (31)	570 (22)	290 (11)
wheat—dry foam	160 (25)	410 (15)	590 (94)	580 (22)	1,040 (44)	690 (58)	400 (17)
HACS—dry foam	110 (9.6)	480 (33)	710 (48)	900 (60)	1,020 (16)	750 (98)	420 (20)
corn/SO	4.4 (2.1)	6.0 (1.1)	34 (5.1)	69 (7.4)	59 (3.3)	270 (57)	25 (3.3)
wheat/SO	1.7 (2.3)	11 (1.6)	58 (3.3)	118 (4.3)	86 (9.7)	370 (42)	51 (1.5)
HACS/SO	2.7 (2.6)	13 (1.6)	85 (6.1)	160 (9.4)	130 (22)	610 (110)	55 (4.7)

[a] The VP values ($\times 10^{-10}$ g m/s m^2 Pa) represent the amount (g) of vapor per unit of time (s) passing through a sample of unit thickness (m) and unit surface area (m^2) and adjusted for vapor pressure (Pa). [b] Values in parentheses indicate standard deviation.

solvent is enveloped in a coating of the carbohydrate material. When the outer coating dries to about 10% (w/w) moisture, it becomes a semipermeable membrane allowing water to pass but becoming impenetrable to the volatile compounds (*30*).

Rankin et al. (*31*) found that starch films had very high transmission rates to water and methanol vapor but were much more impermeable to vapors of a host of other organic compounds. Vapor transport through the films was primarily via a diffusion mechanism as they noted that the starch films were dense and devoid of submicroscopic holes, which accounted for the low permeability to nitrogen and oxygen gases (*31*). In contrast to starch films in which vapor diffuses directly through the film, the dry starch foam used in the present study was comprised of a porous, open cell microstructure through which vapors could pass via mass flow. As a result, the VTR was largely determined by the vapor pressure of the test solvent. This was evident by the high VTR of acetone (high vapor pressure) in dry starch foam relative to water whereas the VTR of water in nonporous starch films was much higher relative to acetone (*31*).

Foam samples saturated with silicone oil had much lower VTR values as compared to the dry foam samples (**Table 2**). Vapor transmission was most likely determined by the properties of the silicone oil, which was by far the largest component of the gel matrix. The transport of solvent vapor through the silicone oil-saturated gel matrix was probably more of a diffusion mechanism rather than mass flow. Solvents that were readily soluble in the silicone oil had the highest VTR. The lowest VTR values were for the polar solvents, water and ethanol, where the VTR values were only 2−4% of the values for the dry foam samples (**Table 2**). The VTR values were higher for acetone, hexanes, and dichloromethane, all of which are less polar, have higher vapor pressures, and are soluble in silicone oil.

VP, a parameter that corrects for the vapor pressure of the solvent, was determined for the dry starch foam and silicone-saturated gels (**Table 3**). The VP values were lowest for water. The low VP values for water may be due, in part, to a sorption/ desorption process of water molecules on the interior surface areas of the starch foam. The overall importance of the sorption/ desorption process is compounded when one considers the high cumulative interior surface area formed by the very fine microstructure of the foam. The lower affinity of nonpolar solvent vapors for the surfaces of the starch foam matrix could also contribute to the higher VP values associated with the nonpolar solvents (**Table 3**).

The mean VP values of the Dent corn samples tended to be lower as compared to the VP values of the HACS samples except for the water vapor treatment (**Table 3**). Lower VP values for the Dent corn samples could be expected based on the differences in density and pore volume among the starch foam samples (**Table 1**). The HACS foam had the lowest density and highest pore volume, which would have facilitated vapor transmission through the foam matrix.

The VP of the silicone oil-saturated gels was at least 1 order of magnitude lower than the VP of the starch foam samples for all solvents tested except for the 2-heptanone sample (**Table 3**). The values were particularly low for the water treatment probably due to the low solubility of water in silicone oil. The VP values were also relatively low for ethanol and acetic acid, which also have limited solubility in silicone oil. In contrast, the VP was higher for the nonpolar solvents, presumably due to their greater solubility in the silicone oil phase.

The highest VP values of the silicone oil-saturated gels were recorded for the 2-heptanone treatment. The VP values were nearly in the range recorded for the dry starch foam samples. Part of the reason for the high VP for 2-heptanone can be attributed to its solubility in silicone oil. However, it is not readily apparent why 2-heptanone would have a higher VP than other nonpolar solvents tested.

The controlled release of volatile chemicals including alcohols, ketones, and even acetic acid has numerous agricultural applications. Particular focus was directed in the present study toward controlled release strategies for 2-heptanone because of its importance as a potent miticide in controlling *Varroa* mite infestation in honey bee colonies. The treatment should be
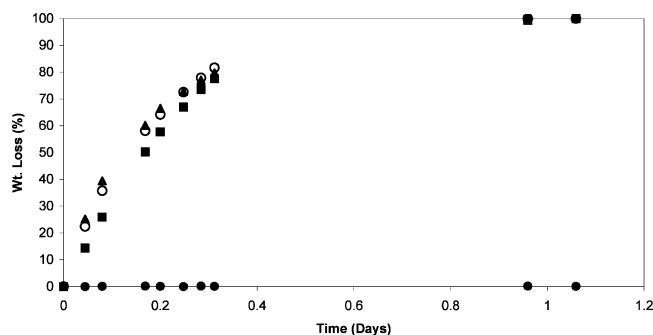
Figure 3. Rate of weight loss (%) for uncoated gels of HACS due to evaporation of 2-heptanone. The liquid in the gel matrix was comprised of 2-heptanone (○), silicone oil (●), or mixtures of 2-heptanone:silicone oil (3:1, ■) (1:3, ▲).

carried out over a complete honeybee brood cycle and preferably over two cycles that span a combined 42 day period to ensure adequate control of *Varroa* mite populations in honeybee colonies (*7*). A target controlled release device could be 5 mm × 25 mm × 185 mm and would fit nicely on the top bars of a commercial honeybee hive. A 2-heptanone-saturated SSG of these dimensions would hold approximately 20 g of 2-heptanone. A flux rate of 4.8×10^{-4} g/s m^2 would be needed to dispense 2-heptanone vapor over the 42 day time period.

On the basis of the VTR data (**Table 2**), a prototype of 0.005 m thickness made of an uncoated HACS gel saturated with 2-heptanone would have a flux rate of 7.2×10^{-3} g/s m^2, which is far higher than the target rate. Even the silicone oil-saturated gel would have a much higher flux rate (5.8×10^{-3} g/s m^2) than the target. These results were verified in experiments with HACS gels saturated with 2-heptanone or mixtures of 2-heptanone and silicone oil (**Figure 3**). The SSG containing only 2-heptanone essentially lost all of the 2-heptanone reserves within a day. The silicone oil did not significantly reduce the rate of 2-heptanone loss in the ranges tested as compared to the sample containing only 2-heptanone (**Figure 3**). The most stable samples were those containing only silicone oil. There was no significant weight loss in samples containing only silicone oil over the time period tested due to the low vapor pressure of silicone oil.

It was apparent from the results that the gel matrix in samples saturated with 2-heptanone was effective in absorbing and holding several volumes of solvent but did not adequately control the release of 2-heptanone for the desired application. It may be that there are other miscible solvents besides silicone oil that could be blended with 2-heptanone and reduce its evaporation rate. However, on the basis of these results, a more viable approach was to use the SSG as a reservoir and to apply a suitable vapor barrier or coating to control the flux rate of 2-heptanone.

The VPs of coating materials including beeswax, paraffin wax, EVOH copolymer, and peach/pectin fruit films were measured (**Table 4**). The wax coatings generally provided excellent barrier properties to water, ethanol, acetone, and acetic acid (**Table 4**). However, the waxes were much less effective barriers for hexanes, dichloromethane, and 2-heptanone. In fact, it was difficult to obtain VP data for hexanes and dichloromethane because the solvent vapors eventually dissolved the waxes and created holes in the coating. As a result, the VP data were based on readings taken before the films were breached, generally less than 48 h. Similarly, the VP of beeswax film for 2-heptanone was based on data collected the first 48 h before

the film breached. The paraffin wax film, however, was more stable to 2-heptanone vapor presumably due to lower solubility.

The EVOH film provided excellent barrier properties for all of the solvents tested but was less effective than the waxes as a barrier to water (**Table 4**). EVOH is a synthetic plastic copolymer that is used in many applications where solvent resistance is needed. EVOH was an effective vapor barrier for 2-heptanone and could be useful in controlled release devices. The resistance of EVOH film to permeability of 2-heptanone vapor was presumably due to the considerable number of hydroxyl groups in the copolymer. The primary concern with using EVOH films for agricultural applications is that the polyethylene component of the copolymer is not readily degraded. Controlled release devices made with EVOH film would most likely need to be recovered once the device was spent.

The fruit film is comprised of pectins and other complex carbohydrates and should be degradable in an agricultural environment. As with starch films (*31*), the fruit film was much more permeable to polar vs nonpolar compounds. The fruit film had the highest VP values of all of the films tested for water, ethanol, and acetic acid. It also had among the lowest VP values for hexanes, dichloromethane, and 2-heptanone. The low permeability to nonpolar solvents is presumably due to the high density of hydroxyl groups in the carbohydrate fraction. As with starch films (*31*), the fruit films may have an increase in intermolecular hydrogen bonding as the films dry, which decreases the permeability of films to solvents.

A bilayer film comprised of beeswax as the outer layer and the fruit film as the inner layer proved to be an effective barrier for both the polar and the nonpolar solvents (**Table 4**). The wax component provided good barrier properties to the water, ethanol, and acetone while the fruit film layer provided good barrier properties to the nonpolar solvents. In addition, the bilayer film was stable and did not develop holes when exposed to the nonpolar solvents over time as did the films composed of only a single layer of wax.

Controlled Release Devices. Small, cylindrical gels saturated with 2-heptanone were prepared and coated with beeswax, paraffin wax, a blend of beeswax:paraffin (1:1), or a fruit film. The wax coating was variable in thickness due to the difficulty in getting the molten wax to adhere to the gel substrate and the need for multiple applications to adequately coat the sample. The relative rate of 2-heptanone release was monitored by recording the percent weight loss over time (**Figure 4**). The sample containing no coating (open triangles) essentially lost all of the 2-heptanone sample within the first day. Samples coated with beeswax (closed squares), a beeswax:paraffin blend (open boxes), or paraffin (closed triangles) released about 60, 20, or 5% of the 2-heptanone reserves over a period of 18 days, respectively. Samples coated with the fruit film had no significant loss of 2-heptanone over an 18 day period (**Figure 4**).

The results of the coating study are generally consistent with the VP tests for the coating materials with the exception that the percent weight loss over time was lower than expected for the beeswax- and paraffin-coated samples. The lower values could be due to the nonuniform thickness of the wax films and the presence of thick areas in the coating, especially in the lower portion of the sample where molten wax tended to accumulate before it solidified.

Beeswax is a natural product and would be a preferred material to use in controlled release devices for honeybees except for its solubility in 2-heptanone. Beeswax is more stable

Starch Gel Matrices

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Table 4. VP of Beeswax, Paraffin Wax, Beeswax:Paraffin Wax Blend (1:1), EVOH, Fruit Film, and Beeswax/Fruit Film Laminate for Vapor of Select Solvents[a]

	water	ethanol	acetone	hexanes	dichloromethane	2-heptanone	acetic acid
beeswax	0.036 (0.0066)[b]	0.026 (0.0021)	0.49 (0.035)	7.0 (2.1)	2.4 (0.27)	138 (20)	0.28 (0.25)
paraffin wax	0.0039 (0.018)	0.0092 (0.0010)	0.23 (0.0072)	6.9 (2.1)	0.72 (0.048)	75 (10)	0.20 (0.10)
wax blend[c]	0.013 (0.0016)	0.031 (0.015)	0.19 (0.029)	4.1 (0.73)	1.7 (0.53)	104 (44)	0.55 (0.23)
EVOH	0.096 (0.0032)	0.0046 (0.00078)	0.023 (0.012)	0.10 (0.018)	0.10 (0.043)	0.029 (0.017)	0.012 (0.0048)
fruit film	2.7 (0.30)	0.26 (0.12)	0.34 (0.075)	0.12 (0.058)	0.020 (0.032)	0.014 (0.0093)	2.3 (0.56)
fruit film/beeswax	0.044 (0.0015)	0.018 (0.0039)	0.14 (0.069)	0.20 (0.12)	0.11 (0.035)	0.69 (0.23)	0.095 (0.0079)

[a] The VP values ($\times 10^{-10}$ g m/s m^2 Pa) represent amount (g) of vapor per unit of time (s) passing through a sample of unit thickness (m) and unit surface area (m^2) and adjusted for vapor pressure (Pa). [b] Values in parentheses indicate standard deviation. [c] The wax blend tested was a 3:2 blend of paraffin and microcrystalline waxes.
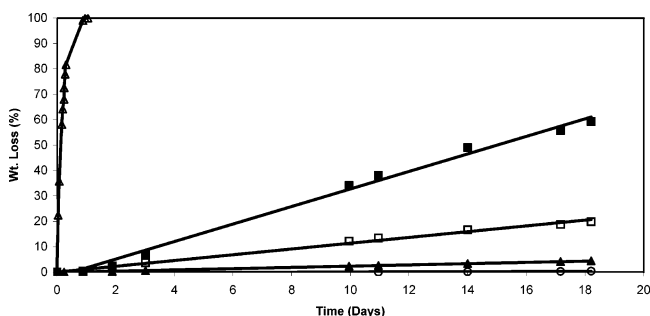
Figure 4. Rate of weight loss (%) for uncoated (△) gels of HACS or gels coated with a film of beeswax (■), paraffin wax (▲), a blend of beeswax and paraffin (1:1; □), or fruit film (○).
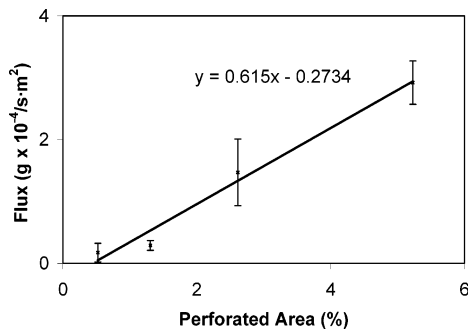
Figure 5. Flux rate of 2-heptanone through laminate of beeswax and fruit film with perforated area ranging from 0.5 to 5%. The flux increased with a greater perforated area ($R^2 = 0.98$); error bars = STD.

as a coating when the 2-heptanone is diluted with silicone oil (**Figure 4**). However, it is preferable to load the starch gels only with active ingredient to maximize the amount loaded and minimize the size of the device. The fruit film/beewax laminate was attractive because the fruit film component limited exposure of the beeswax with the 2-heptanone and the beeswax component limited exposure of the outer surface of the fruit film to moisture.

A series of samples with a 2-heptanone-saturated SSG core and a fruit film/beeswax laminate coating were monitored over time. The fruit film component was perforated to different degrees to provide a range in the flux rate of 2-heptanone (**Figure 5**). The results show an increase in flux with increasing perforated area. As mentioned earlier, a flux rate of 4.8×10^{-4} g/s m^2 would be needed to deliver the 2-heptanone vapor over a 42 day period based on the dimensions (5 mm × 25 mm × 185 mm) of a target device. The fruit film component of the laminate would need a perforated area of approximately 8.2% to provide the target flux rate for a target device. Further work may focus on making carbohydrate films formulated with greater VPs to 2-heptanone to obviate the need to perforate the film component of laminate films.

Conclusion. The controlled release of volatile agrochemicals is important in effectively controlling pests that are economically important. A wide range in vapor flux rates can be attained for a given solvent by using dry starch foam, SSG, or by using SSG as a reservoir combined with various films or coatings. Particular emphasis was placed on achieving target flux rates for 2-heptanone in the present study. However, similar methods can be used to control the vapor flux for a wide range of biologically active solvents. The results show that effective controlled release devices could be made using agricultural materials. Devices made of agricultural materials would have an advantage over conventional devices because they are derived from renewable resources, and if they are biodegradable, they can be left in the field when spent.

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