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Evaluation of Silica Sol-Gel Microcapsule for the Controlled Release of Insect Repellent, *N,N*-Diethyl-2-methoxybenzamide, on Cotton

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N,N-diethyl-2-methoxybenzamide, an insect repellent compound, was incorporated into cotton textile using the sol-gel method. Evaluation of the results of four different sol-gel formulations showed that a lower condensation rate resulted in significantly better encapsulation. Also investigated was the encapsulation in the presence of other polymers like polymethylmethacrylate (PMMA), polystyrene (PS) and polyvinyl alcohol (PVA) that prolong the release of the repellent. The sol-gel formulation, SiO₂: polymethylmethacrylate (PMMA) (1:0.8), gave smooth fabric and good encapsulation of the insect repellent compound. PS and PVA resulted in cloths which are aesthetically undesirable. Cloths coated with sol-gel PVA gave the best repellent release profile.

Key Words: functionalized textile, *N,N*-diethyl-2-methoxybenzamide, sol-gel

INTRODUCTION

The sol-gel process is a versatile solution technique for encapsulating and depositing functional compounds on different materials (Penard et al. 2007; Trewyn et al. 2007). The process typically involves the hydrolysis of inorganic metal salts or metal-organic compounds such as metal alkoxides, forming a colloidal suspension or sol. The sol subsequently polymerizes forming a wet gel. Heat is applied to remove the solvent, yielding a ceramic material (Figure 1) (Veith et al. 2005).

Recent research has shown that the sol-gel method can be used to fabricate a variety of new materials such as thin-film coatings (Tshabalala et al. 2003), ceramic-coated fibers (Zhou et al. 1997), microporous inorganic membranes (de Lange et al. 1995), monolithic ceramics and glasses (Siouffi 2003), and extremely porous aerogel materials (Hench and West 1990). This method can be used to create sol-gel thin films for the encapsulation of insect repellents on cloth.

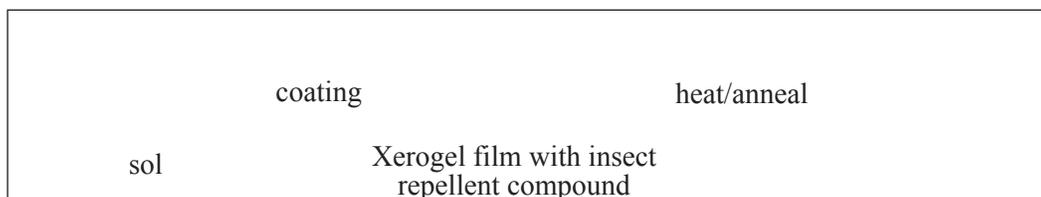


Figure 1. Sol-gel process in the presence of insect repellent compound: The inorganic salt is hydrolyzed to form a sol. The repellent compound is added to the sol, and the cloth is coated by dip method. Heat is applied to the coated material to anneal.

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In this study, the transport kinetics of sol-gel encapsulated insect repellent, *N,N*-diethyl-2-methoxybenzamide, deposited on cotton cloth was studied by varying the hydrolysis ratio (the molar ratio of water to Tetraethoxysilane, TEOS) and base concentration. The addition of commercial polymers polymethylmethacrylate (PMMA), polystyrene (PS), and polyvinyl alcohol (PVA) to the sol prior to sol-gel deposition on cotton was also investigated to prolong the release of the repellent (Böttcher et al. 1999; Quellet et al. 2001).

MATERIALS AND METHODS

Synthesis

The starting material, salicylic acid, was obtained from Fluka. Iodomethane (CH_3I), 4-dimethylaminopyridine (DMAP) was obtained from Merck, and dicyclohexylcarbodiimide (DCC) was obtained from Sigma-Aldrich. All of these materials were used without further purification. Dichloromethane (DCM) was dried over calcium sulfate and distilled. Tetrahydrofuran (THF) was dried over sodium metal and benzophenone and then distilled. Diethylamine was refluxed with KOH and then distilled. Hexane and ethyl acetate (EtOAc) were distilled before use. Sodium hydride (NaH) was washed in hexane to remove the mineral oil coating, dried, and then used immediately in the synthesis. Merck silica gel 60 f254 was used for thin layer chromatography (TLC) and Merck-7729 silica gel was used for column chromatography. The repellent compound, *N,N*-diethyl-2-methoxybenzamide, was analyzed using a Shimadzu FTIR-8201 PC Fourier-Transform Infrared (FTIR) Spectrophotometer and JEOL LA 400 MHz Nuclear Magnetic Resonance (NMR) spectrometer.

Formation of the sol-gel coating

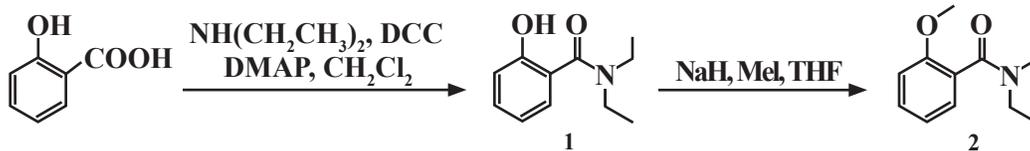
Tetraethoxysilane (TEOS, Reagent Grade, 98%) was purchased from Sigma-Aldrich and ethanol (99%) was obtained from Merck. The monomers, methyl methacrylate (MMA) and styrene, were purchased from Sigma-Aldrich and Polymer Products Philippines, Incorporated, respectively. The monomers were purified by distillation before use. Polyvinyl alcohol (PVA, MW

72,000) was purchased from Merck. A Shimadzu GC-14B flame ionization detector with column (J and W Scientific DB 1701) was used to analyze textile extracts. The samples were analyzed using a column temperature ramping of $5^\circ\text{C}/\text{min}$ starting from 80°C to 210°C . The injector temperature was 220°C and the detector temperature was 230°C . Under these conditions, *N,N*-diethyl-2-methoxybenzamide has a retention time of 20-21 minutes. Thermogravimetric analysis experiments were done using a Shimadzu DT60H TGA/DSC instrument. Surface analysis was carried out using a JEOL JFC 1200 fine gold coater and a JEOL JSM 5310 Scanning Electron Microscope.

Synthesis of *N,N*-diethyl-2-methoxybenzamide

N,N-Diethyl-2-hydroxybenzamide (**1**). Amidation was done using a modified procedure by Barlett (Barlett et al. 2006) and Neises (Neises & Steiglich 1990). DMAP (1.10 g, 9.00 mmol) was added to a solution of salicylic acid (1.71 g, 12.4 mmol) and diethylamine (0.63 g, 8.61 mmol) in dry DCM (50 mL). After stirring for five minutes, DCC (2.49 g, 12.1 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. The precipitate was removed by filtration and the filtrate was washed successively with 10% NaHCO_3 (80 mL X 2), water, and brine then dried over Na_2SO_4 . The solvent was evaporated and the crude product was purified by column chromatography (99:1 hexane/EtOAc to EtOAc) to give a yellow oil (0.72 g, 43%): $R_f = 0.371$, 20:80 EtOAc/hexane; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.25 (t, $J = 7.08$ Hz, 6H), 3.5 (q, $J = 7.08$ Hz, 4H), 6.75-8 (m, 4 H); IR (neat): 3217, 2985, 2939, 1672, 1606, 1485, 1461, 1386, 1365, 1299, 1247, 1218, 1157, 757 cm^{-1} .

N,N-Diethyl-2-methoxybenzamide (**2**) (Olsher et al. 1999). Amide **1** (0.50 g, 2.6 mmol) was dissolved in dry THF (14 mL). NaH (0.93 g, 39 mmol) was added to this solution at 0°C . After stirring for 1 h, iodomethane (0.50 mL, 8.0 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 17 h at room temperature. Water (5 mL) was added dropwise to destroy the excess NaH. The solvent was evaporated and the residue was dissolved in dichloromethane (10 mL). The organic layer was washed with water (10 mL), dried with Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (99:1 hexane/chloroform then



Scheme 1. Synthesis of *N,N*-diethyl-2-methoxybenzamide

EtOAc) to provide a light brown viscous oil (0.37 g, 69%): R_f = 0.228, 20:80 EtOAc/hexane; ¹H NMR (400 MHz, CDCl₃) δ 1.02 (t, *J* = 7.08 Hz, 3H), 1.25 (t, *J* = 7.08 Hz, 3H), 3.10 (s, 3H), 3.16 (q, *J* = 7.08 Hz, 2H), 3.55 (q, *J* = 4.88 Hz, 2H), 6.75-7.4 (m, 4H); IR (neat) 2977, 2939, 1635, 1506, 1475, 1434, 1382, 1375, 1296, 1276, 1247, 1182, 1089, 1024, 757 cm⁻¹.

Preparation of the Sol-gel

Four different sol-gel formulations were prepared using procedures adapted from Veith and co-workers (2004) (Table 1). For each formulation, tetraethyl orthosilicate (TEOS), hydrochloric acid solution (HCl), ethanol and deionized (DI) water (conductivity=0.1 μS/cm) were mixed at room temperature (~pH 2). This solution was covered and stirred for 48 h. Sodium hydroxide was added to the mixture to induce gelation (~pH 6-7).

Table 1. Sol-gel formulations used

| | A | B | C | D |
|-------------------------|-------|-------|-------|-------|
| TEOS (mol%) | 8.7 | 8.7 | 2.4 | 2.4 |
| Ethanol (mol%) | 47.4 | 47.4 | 37.3 | 37.3 |
| HCl (mol%) | 0.047 | 0.047 | 0.065 | 0.065 |
| H ₂ O (mol%) | 43.9 | 43.9 | 60.3 | 60.3 |
| NaOH (M) | 0.9 | 0.09 | 0.9 | 0.09 |

Cotton (100%) cloth samples (8x1 inches swatch strips) were prepared in duplicates. The strips were pre-treated by immersion in 0.9 M NaOH solution for 24 h and air-dried. TEOS, ethanol, DI water, and hydrochloric acid solution were mixed at room temperature for 48 h. Sodium hydroxide was added to the mixture until it reaches pH 3.5 level. To this, *N,N*-diethyl-2-methoxybenzamide was added, after which, the pre-treated cloth was dipped into the mixture and allowed to air-dry for 10 min. The partially dried cloth was heated in a vacuum oven at 60° C and 750 mbar for 24 h. SEM analysis was carried out by cutting a 2x2 mm of cloth sample before washing.

Study of the retention and release of repellent compound on sol-gel coated cloth

Three effects related to the retention and release of the repellent compound, *N,N*-diethyl-2-methoxybenzamide, were studied. These include the number of dips, hydrolysis ratio and base concentration, and the addition of polymer.

Coating

The number of coating in terms of dips was investigated in order to know if this will affect the release of the

repellent. In this study, the effect of two and five dips was investigated.

Hydrolysis ratio

High base concentration can result to the rapid formation of the sol-gel particles. This will have an effect on the porosity of the matrix and the ease of release of the repellent.

Addition of polymer

We wanted to investigate the effect of adding hydrophobic systems like PMMA and the amount needed to achieve good retention and release of the repellent. Furthermore, other polymers like PS and PVA will also be investigated.

For samples that contain polymethylmethacrylate (PMMA), the monomer (5.0 mL, 47.2 mmol) was first polymerized with benzoyl peroxide (0.80 g, 3.30 mmol) for one hour. After hydrolysis, varied amounts of the monomer was added to the TEOS mixture to provide different mixtures of SiO₂:PMMA molar ratios (1:0.8, 1:0.6, 1:0.5, 1:0.4, 1:0.2). The mixture of monomer and TEOS was stirred for one hour before the addition of the base. Subsequent steps to prepare the sol-gel mixture is described (*vide supra*). Other polymers PS and PVA were incorporated similarly as PMMA.

To quantify the release of the insect repellent compound *N,N*-diethyl-2-methoxybenzamide it was extracted from a previously-treated encapsulated sol-gel cloth (cut 1x1 inch from the 8x1 inch swatch). The 1x1 inch sample was subjected to ethyl acetate extraction for 2-3 hours (Veith et al. 2005). The extract was collected, placed in a volumetric flask, and diluted in 5.00 mL of additional ethyl acetate solvent. A 1.00 μL sample was injected to the gas chromatography column (GC) for analysis. For each formulation used as a coating (See Table 1), two GC analysis were conducted. The concentration of the *N,N*-diethyl-2-methoxybenzamide extracted from the swatch was reported as the percent mass ratio of repellent released in ethyl acetate extraction over the mass initially placed in the sol-gel coating solution.

Degree of retention of *N,N*-diethyl-2-methoxybenzamide

The amount of the repellent compound retained on the cloth sample (R_c) was determined by taking the difference between the total amount of compound in the sol solution (R_t) and the sum of the of the total amount of repellent in the sample dipping container after dipping (container, R_c) and the amount of repellent extracted before washing (0 wash, R_w) (Repellent on cloth, R_t = R_c - (R_c + R_w)). Washing was conducted by brushing the strip with soap solution 10 times on both sides and drying. A standard calibration

curve was used to extrapolate the amount of compound in the extract.

A control experiment using an uncoated fabric was also carried out. The results showed that significant amount of compound can be extracted from the cloth before washing (0 wash). However, after the first wash, no more compound was extracted from the samples. This suggests that retention of the insect repellent compound to the cloth is better in the presence of sol-gel. In order to further assess and improve the binding properties of the encapsulated sol-gel we also investigated the addition of several known polymers to sol-gel formulations.

RESULTS AND DISCUSSION

The cotton cloth coated with four sol-gel formulations were evaluated according to appearance, release rate, and retention. Formulations A and C (with 0.9 M NaOH) showed faster gel formation. The resulting coated cloth was rough to touch and granulated silica particles were also observed on the surface of the cloth. Cloths coated with formulation B were slightly stiff, but the cloths were smooth and non-granular.

In order to evaluate the performance of the different formulations, the effects of three other factors were explored: first, the effect of number of coatings - two versus five dips; second, the effect of the hydrolysis ratio and base concentration; and finally, the effect of addition of PMMA and the amount needed to achieve a good retention and release of the repellent. Once the optimal ratio of the polymer and sol-gel was determined, we looked at two other different polymer systems.

In terms of the number of coating, the cloth samples that were dipped five times became stiffer than those that were dipped twice. Furthermore, the cloth samples that were dipped twice resulted in the facile release of the insect repellent compound for formulations A, B, and C (Figure 2). Comparing the two, the samples that were dipped five times gave better results in terms of compound retention.

From Table 1, Formulas A and C have high base concentration which resulted in the rapid formation of the sol-gel particles. A white granular material, instead of the thin film formation on the surface of the cloth, was observed. Consequently, this resulted in weaker adhesion of the sol-gel to the cloth surface and retention of less compound. Textiles obtained using Formulas B

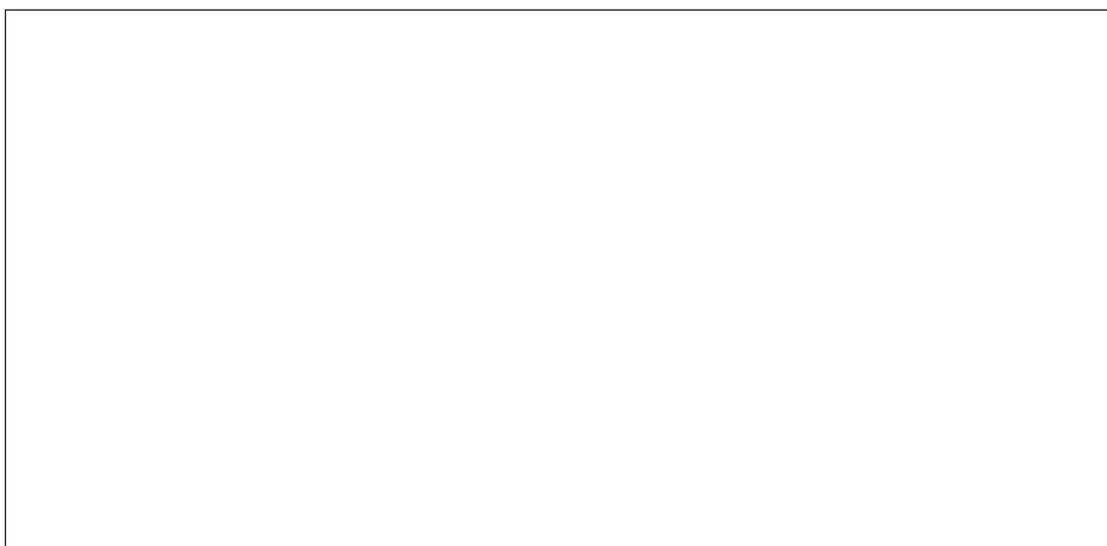


Figure 2. The mass % of insect repellent, *N,N*-diethyl-2-methoxybenzamide, extracted from cotton using different sol-gel formulations and number of coating (two and five dips)

Samples were in the form of 1 x 1 inch cotton fabrics (samples were dip-coated)
legend: 0 was=before washing, 1 wash=after washing once

and D resulted in a higher amount of repellent compound extracted than the other formulations before washing (0 wash). Comparing B and D, Formula D has a larger pore percentage and volume due to lower TEOS/water ratio and base concentration. Thus, the repellent compound could still be extracted from D (five dips).

After the first wash, the amount of repellent compound extracted generally decreased for all samples regardless of the number of dips or formulations. This could indicate two possibilities. First, the compounds adhered on the surface of the cloth were washed away and only a small amount remained on the cloth. Second, the repellent compound is effectively encapsulated in the sol-gel matrix and cannot be easily released. Thus, the addition of polymeric systems such as PMMA to the sol-gel mixture was further studied on how they affect the retention.

Previous studies on the use of 30% PMMA in silica sol-gel coated on cotton showed superior retention of the repellent compound diethyltoluamide (DETA) compared with silica coated samples (Mahlting et al. 2005). However, there were no studies on the optimum amount of PMMA incorporation. Here, it is important to

note that a good formulation should allow the retention as well as the release of the insect repellent compound.

In our study, the amount of extracted repellent compound in the presence of PMMA (1:0.5 molar ratio of SiO_2 :MMA, Figure 3) was less compared with the cloths coated with sol-gel (Figure 2). Furthermore, it is worth noting that comparing Formulas B and D with and without PMMA (Figure 3 and 2) with Formulas A and C, a better and more consistent release profile was observed in the former formulations. Specifically, in the presence of PMMA (Figure 3), no compound was extracted from A and C (five dips).

Because of smooth fabric appearance of Formula B and the superior retention and release of the formula in the presence of PMMA, this formula was further explored by varying the PMMA ratio. All the experiments were done with five dips. Several SiO_2 :MMA molar ratios were used (PMMA, 1:0.8, 1:0.4, 1:0.2) (Table 2). The mass of compound in both the cloth and the dipping container were measured in order to account for the distribution of the compound and to verify its encapsulation in the sol-gel matrix.

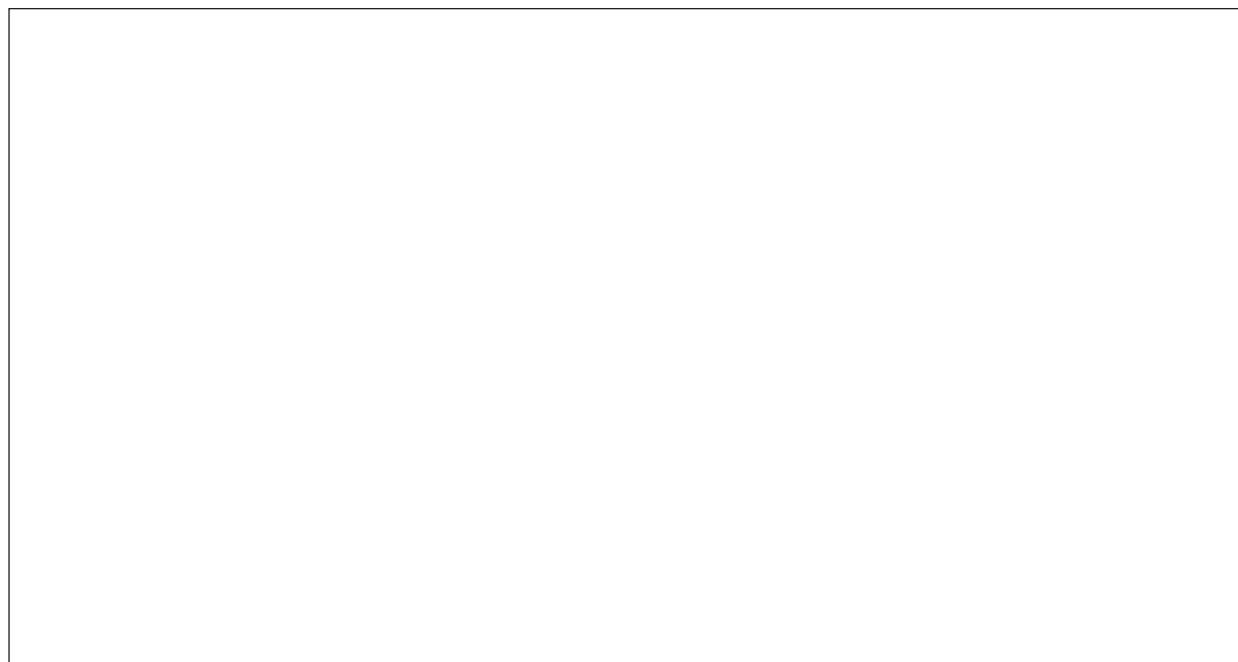


Figure 3. The mass % of *N,N*-diethyl-2-methoxybenzamide extracted from samples with different sol-gel formulations with PMMA (1:0.5 molar ratio of SiO_2 :MMA)

Samples were in the form of 1 x 1 inch cotton fabrics (samples were dip-coated)
legend: 0 was=before washing, 1 wash=after washing once

Table 2. Mass percentage of repellent compound retained and released from the samples coated with sol-gel formula B and PMMA (1:0.8, 1:0.4, 1:0.2)

| Source | PMMA | 01:00.8 | 01:00.4 | 01:00.2 |
|--|--------|---------|---------|---------|
| Container ^a | 16.859 | 40.580 | 43.995 | 88.075 |
| Cloth before washing (0 wash) | 0.099 | 0.453 | 0.581 | 0.464 |
| Repellent retained on cloth ^b | 82.351 | 55.795 | 51.360 | 8.214 |
| 1 wash ^c | 0 | 0.133 | 0.070 | 0.028 |
| 2 wash ^c | 0 | 0.022 | 0.024 | 0.007 |
| 3 wash ^c | NA | 0.021 | 0.006 | 0 |

a: taken in two extractions from the powdered silica gel left in the container, this is also the amount not incorporated in the sol-gel matrix

b: retained in cloth due to the sol-gel matrix; Retained=100%-(compound in container+amount on swatch strips before washing). Repellent on cloth, $R_t = R_c - (R_1 + R_2 + R_3)$

c: amount of cloth after washing, measured as an average between two samples (1X1 cm swatch)

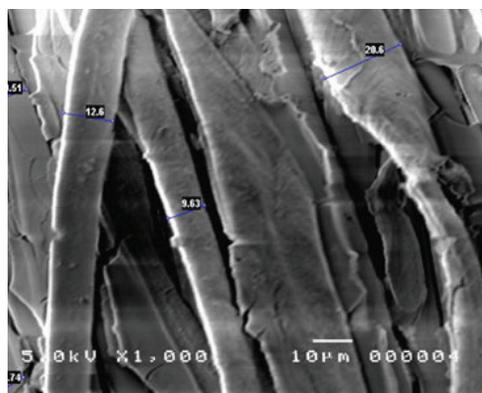
In order to account for the mass balance, each entry was reported as mass percent, which refers to the mass of repellent released in ethyl acetate extraction over the mass initially placed in the sol-gel coating solution expressed in grams. The PMMA stands for the cloth with sol-gel PMMA coating; 1:x (where x= 0.8, 0.4, 0.2) stands for the sol-gel formula B with x amount of PMMA molar equivalent. The container stands for the amount of repellent remaining in the sol-gel dipping mixture. It is also the amount not incorporated in the sol-gel matrix. The amount of repellent before washing the strip is termed “0 wash,” after the first wash it is called “1 wash”, and so on. The amount of repellent retained on the cloth is the difference between the total amount of repellent used and the amount extracted from the container and 0 wash.

Comparing the PMMA ratio in Table 2, the amount of repellent compound that was not incorporated (left in the container) was higher by B:0.2 PMMA compared with the other PMMA ratios. The lower ratio of PMMA in the mixture provided a matrix that is less hydrophobic. As a result, the

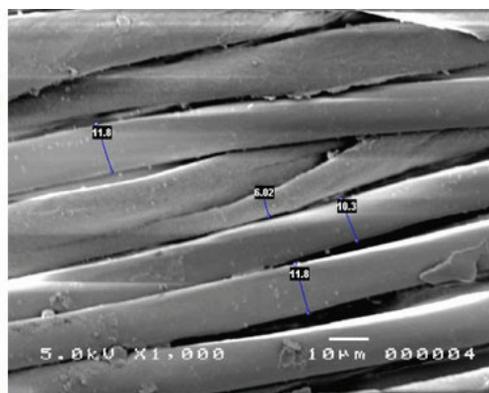
compound was less efficiently encapsulated. The sample with the higher amount of PMMA (0.8 PMMA) resulted in better encapsulation of the compound. Furthermore, the results of the wash also showed that the fabric with 0.8 PMMA exhibits controlled repellent release even after the third wash. Except for 0.4 PMMA, other formulations stopped releasing the repellent after the third wash.

The amount of repellent released was also compared before washing (0 wash) and after subsequent washings. In the absence of sol-gel, PMMA (Table 2) allowed good encapsulation of the repellent. However, no compound was released after the first wash. The results obtained are also consistent with the report of Böttcher which proposes two processes involved in the release of encapsulated organic liquid- a fast liberation process and a slow diffusion of the remaining liquid (Böttcher et al. 1999). In the table, it can be seen that the repellent compound that adhered only on the surface of the cloth was extracted more easily. This can be observed in the entry before washing (0 wash) in which considerable amount of compound was extracted from the textile. After the first wash, the subsequent amount of the compound extracted was significantly lower and was steady within a certain range of values, indicating the slow diffusion of the remaining compound from the porous network.

In order to evaluate the surface of the textile and the amount of compound encapsulated in the coating, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) of the samples were obtained. The SEM of the blank textile and the textile coated with Formula B and 0.8 PMMA are shown in Figure 4. In the 0.8 PMMA, it is evident the silica layer was evenly coated on the surface of the textile allowing the encapsulation of the compound. While in the TGA analysis of Formula B with 0.8 PMMA, there was an incorporation of low boiling compound (Figure 5). The temperature (28–325°



B: 0.8 PMMA



Blank

Figure 4. Scanning electron microscopy (SEM) of blank and formula B with 0.8 PMMA cloth

C) can be attributed to the steady loss of the repellent. At a higher temperature (325° C and above), PMMA and cellulose are degraded and only the silicates remained after 500° C. Furthermore, the sample with a higher

PMMA ratio showed greater mass loss (Figure 6). This result correlates with the previous observation from Table 2 that higher amount of PMMA allows more repellent to be encapsulated.

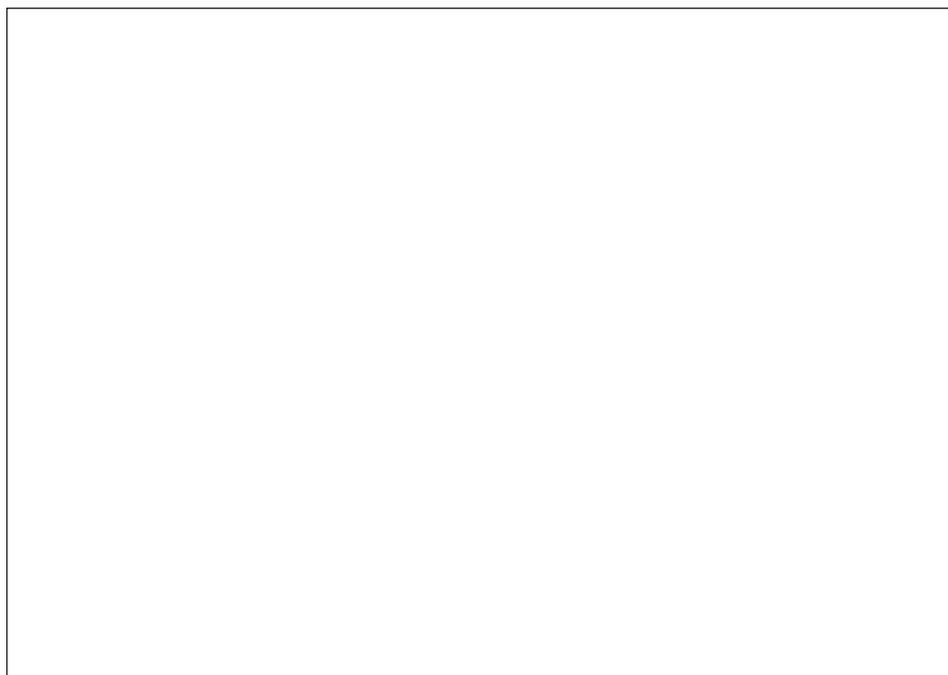


Figure 5. Thermogravimetric analysis (TGA) profile of cloth (formula B with 0.8 PMMA)

*Temperature program: rt-50° C (2° C/min); 50-120° C (5° C/min), hold 10 min; 120-350° C (10° C/min); hold 5 min; 350-500° C (20° C/min)

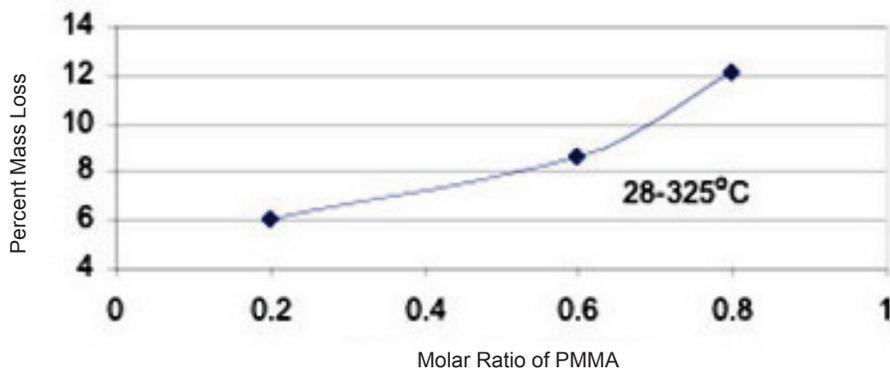


Figure 6. Thermogravimetric analysis (TGA) plot of repellent release in sol-gel samples containing 0.8, 0.6, 0.2 PMMA

In a study reported by Mahltig and co-workers (2005), the use of hydrophobic system like PMMA with *N,N*-diethyl-meta-toluamide (DEET) resulted in the controlled release of the compound. Addition of polymer system like PMMA was reported to improve the retention and release of the encapsulated compound (Mahltig et al. 2005). In our study, the performance of the other polymers such as polystyrene (PS) and polyvinyl alcohol (PVA) in the retention and release of the insect repellent from the coating was also evaluated aside from PMMA.

In terms of appearance of the cloth samples coated with solgel and different polymers, the surface of the cloth obtained using PS is granular compared with PMMA. However, cloth samples with PVA are rough and aesthetically undesirable.

In general, better encapsulation and release is evident for the textile samples with sol-gel and polymer coating. In the absence of polymer (Table 3), no repellent was extracted from the textile after the third wash. From Table 3, it is clear that the coating that does not contain any polymer (entry B) is unsuitable for repeated washing because the repellent compound was easily washed off. Comparing the different polymer system in this study with *N,N*-diethyl-2-methoxybenzamide, the most hydrophobic of the three, PS, resulted to good repellent retention. However, the release profile is not as good as PVA coated textile. While PVA, the most hydrophilic of the three, gave modest retention and allowed the slow release of the repellent even after the fifth wash (Table 3, 5th wash).

Comparing the different polymer system in this study with *N,N*-diethyl-2-methoxybenzamide, the most hydrophobic of the three, PS, resulted in good repellent retention.

Table 3. Percentage of repellent compound retained and released from the sol-gel coating in the presence of PMMA, PVA and PS

| | B | B-0.8PMMA | B-5%PVA | B-0.8PS |
|--|--------|-----------|---------|---------|
| container ^a | 25.723 | 27.843 | 28.183 | 28.626 |
| Cloth before washing (0 wash) | 4.758 | 1.293 | 2.569 | 1.637 |
| Repellent retained on cloth ^b | NA | 22.553 | 30.711 | 45.179 |
| 1 wash ^c | 1.552 | 0.311 | 0.724 | 0.307 |
| 2 wash ^c | 0.093 | 0.193 | 0.432 | 0.201 |
| 3 wash ^c | 0 | 0.229 | 0.281 | 0.085 |
| 5 wash ^c | 0 | 0 | 0.102 | 0 |

a: taken in two extractions from the powdered silica gel left in the container, this is also the amount not incorporated in the sol-gel matrix

b: retained in cloth due to the sol-gel matrix; Retained=100%-(compound in container+amount on swatch strips before washing). Repellent on cloth, $R_c = R_i - (R_s + R_{s'})$

c: amount of cloth after washing, measured as an average between two samples (1X1 cm swatch)

However, the no repellent compound was obtained after the third wash. While PVA, the most hydrophilic of the three, gave modest retention and allowed the slow release of the repellent even after the fifth wash (Table 3, 5th wash).

It is apparent here that the type of polymer incorporated into the sol-gel matrix affects the rate of retention and release of the encapsulated repellent compound. Hence, it is important to find a polymer system that exhibits a slow decrease in extracted compound to prolong the use of the insect repellent fabric. Here, even though PVA sol-gel coating resulted in cotton cloths with rough texture, it provided the most promising result in terms of retention and release.

CONCLUSION

Insect repellent cotton cloths were prepared using the sol-gel technique. This method is effective in depositing and encapsulating the insect repellent compound *N,N*-diethyl-2-methoxybenzamide on cotton. The overall performance and appearance of the coated textile depended on the formulation used. Formulations which made use of high base concentrations (A and C) resulted in a grainy textile surface while the use of low base concentrations (B and D) led to smoother thin-film coatings. Increasing the number of coatings yielded stiffer fabrics and greater overall retention of the repellent compound. Other factors that contributed to a good functional textile were formulations with high ratio of TEOS/water and low initial pH level. Furthermore, the addition of the hydrophobic system like PMMA can enhance the retention as seen in the sol-gel mixture, SiO₂:PMMA (1:0.8).

Textiles coated with sol-gel in the presence of PS provided slightly rough fabric and poorer retention and release compared with PMMA. The results obtained with PVA were superior to PMMA, but the appearance of the sol-gel/PVA-coated textile is undesirable. Further studies are required to improve the appearance of PVA in sol-gel textile coating.

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