J. Rubb. Res., **17(3)**, 173–186

Assessments of Capsaicin Incorporated Silicone Rubber as Antifouling Coatings

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Capsaicin, a natural pepper extract that is substantially less toxic than most currently used antifoulants such as organotin compounds, could be a potential environmentally friendly antifoulant. The antibacterial effectiveness of capsaicin has been reported. However, no detailed study on incorporating the compound into silicone coatings has been conducted. In this study, capsaicin was incorporated into silicone coatings to achieve a synergistic effect by combining the antifouling properties of capsaicin with the foul release performance of silicone rubbers. The silicones used were polydimethylsiloxane rubbers with two different curing mechanisms. Due to the poisonous effect of capsaicin to Pt-based catalysts used for hydrosilylation curing of some silicone coatings, a swelling technique of precured coatings in the capsaicin/benzene solution was utilised. For silicone cured with tin-based catalysts, whose catalysis capability was unaffected by capsaicin, capsaicin was blended into the coating in the presence of a common solvent. Surface and bulk properties of the capsaicin-incorporated coatings were controlled closely to those of the silicone coatings alone, thus minimising their contribution to antifouling. The bacterial attachment studies indicated that all capsaicin-incorporated coatings exhibited initial enhancement in antibacterial performance as compared to coatings containing no capsaicin. However, due to the fast leaching of capsaicin and the adverse effect of the increase surface roughness upon water immersion, the antibacterial effectiveness for capsaicin incorporated coatings only exhibited for a short period of time.

Keywords: Antifoulant; capsaicin; silicone rubber; antifoulant leaching; surface properties

Marine biofouling, the accumulation and growth of marine organisms on the surfaces of infrastructures immersed in natural water, is a serious problem in the maritime industry[1]. The layer of attached organisms on ships hulls decreases ship's speed and mobility and subsequently increases fuel consumption and maintenance costs[2]. Biofouling is also directly associated with the biocorrosion and other related health and environmental problems[3].

The process of biofouling begins with a thin conditioning film, consists mainly of different proteins and dissolved organic matters, formed minutes after a surface is immersed in water. It is followed by the attachment of

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single floating bacteria, which once firmly attached starts to generate extracellular polymeric substances (EPS). EPS connects the cells together and adheres strongly to the surface to form biofilm that makes the surface more attractive to higher level foulers[4]. The conditioning step is unavoidable for any kind of surface immersed. Therefore, an effective strategy to minimise biofilm formation and the subsequent macrofoulers attachment is to prevent or reduce bacterial adhesion.

Toxic compounds, either heavy metal based or organic, have long been incorporated into coatings to prevent biofouling by killing off the attached organisms. Unfortunately, these compounds are also toxic against non targeted organisms[5]. Environmental concerns have proposed the reduction or a complete ban on the use of these compounds[6]. Currently, considerable efforts are being pursued in the search of non toxic antifouling alternatives, including foul release coatings made of lower surface energy materials[7–8] or coatings incorporated with environmentally benign natural product antifoulants (NPAs)[9–11].

Among the environmentally benign NPAs is capsaicin, a stable monoclinic crystalline alkaloid extracted from chilli peppers, is being considered as a potential. Capsaicin or 8-methyl-N-vanillyl-6-nonenamide and its analogues have been used as active ingredients in medicines and found to be effective in inhibiting bacterial growth[12–14]. The presence of capsaicin in an aqueous solution was found to reduce the bacterial attachment on a coating[15–16]. In addition, many patents[17–18] and research papers[19–21] have documented the effectiveness of capsaicin-filled paints against micro and macrofouling organisms. Moreover, capsaicin is significantly less toxic (EC_{50}, the concentration to eliminate 50% of bacterial population, is ~ 5 to 20 p.p.m.) towards various bacteria[16] as compared to organotin compounds (EC_{50} < 0.01 p.p.b.). Furthermore, capsaicin is biodegradable in the marine environment[22] and approved by the Environmental Protection Agency (EPA) as an active ingredient for insect, bug and animal repellents. Therefore, it is an attractive candidate to be utilised for generating environmentally benign coatings.

However, based on our knowledge, the incorporation of capsaicin into a foul release coating such as silicone, has not been attempted. If capsaicin could be incorporated into a foul release coating, a synergistic effect, wherein the antifouling properties of capsaicin which are able to be combined with the foul release performance of silicone can be acquired. Attributable to its unique structures, silicones have been considered as one of the most attractive foul release marine coatings. They consist mostly of polydimethylsiloxane (PDMS), which has methyl ($–CH_3$) side chains resulting in its low surface energy (~ 22 mJ/m^2) and a flexible, inorganic -Si-O backbone linkage leads to its extremely low elastic modulus[7]. Both are essential to the extremely low adhesion associated with silicone coatings. In the current paper, two types of silicones, having different curing mechanisms, were utilised as the coating carriers for capsaicin to be incorporated in.

Specifically, the focus of this work was to investigate different means of incorporating capsaicin into two silicones, Sylgard™ 184 and RTV11 as well as to assess the antibacterial performance of capsaicin-treated coatings. Although the surface immobilisation technique appears to be attractive for retaining capsaicin molecules permanently to the coating surface for the long term antifouling service of the coating, it has been shown that it was very challenging to chemically graft capsaicin molecules onto the surface of silicone directly[23–24]. The leaching of capsaicin from coating matrix was also determined in the current study to address the service life and usefulness of capsaicin blended silicone

coatings. The antibacterial performance of the capsaicin incorporated coatings was assessed by bacterial attachment studies in water containing either enriched Lake Erie bacteria or *Pseudomonas putida*.

MATERIALS AND METHODS

Materials

RTV11 and Sylgard™ 184 were purchased from GE and Dow Corning, respectively. RTV11 came from the manufacturer in two parts: A polymer base (a hydroxy-terminated PDMS) and a catalyst (Dibutyltin dilaurate or DBT). Included in the polymer base are the crosslinking agent (ethyl silicate 40) and the filler (calcium carbonate). Sylgard™ 184 also came in two parts: A polymer base containing vinyl-terminated-PDMS and a curing agent having SiH-terminated-PDMS and the Pt-catalyst. Capsaicin (a naturally extracted mixture containing approximately 65% capsaicin and 35% dihydrocapsaicin) was purchased from Sigma and Aldrich Chemical Inc. and used as received. HPLC grades of benzene, toluene and acetonitrile were purchased from VWR and also used as received. Microscopic glass slides were obtained from VWR.

The two silicone rubbers used in this study were commercial grades and used as received without any modifications. Sylgard™ 184 was a model system and had the advantage of being highly transparent (since it came without fillers) and thus, it would be easy to observe the dispersion of capsaicin aggregates inside the matrix by optical microscope. On the other hand, RTV11 was more practical in the coating industry because it came with high content of strengthening filler (32 wt% $CaCO_3$), but was opaque and therefore, it would not be possible to observe the capsaicin aggregates inside the matrix by optical microscope.

From the manufacturer data sheet, the following properties were obtained for capsaicin, chemical formula: $C_{18}H_{27}NO_3$, molecular weight: 305.41 g/mol, melting point: 62–65ºC and boiling point: 210–220ºC. It was freely soluble in benzene, toluene, ethanol, chloroform, acetonitrile and ether. It came in a form of crystalline white powder.

Coatings Preparation and Processing

Capsaicin was first dissolved in toluene at a concentration of 4 wt%. For producing RTV11 sheets with 1 wt% capsaicin incorporated and at 20:80 (solvent: polymer) mass ratio, 1.5 g of the 4 wt% capsaicin/toluene solution was homogenised with 6 g of RTV11 base with thorough mixing. The mixtures were left inside the fume hood at ambient conditions for 2 days, and then placed under vacuum at room temperature for 20 min to remove the solvent. After that, 0.03 g DBT catalyst was added to the mixture and thoroughly mixed, thus producing 0.5 wt% of DBT. The mixture was poured into a 9 cm diameter polystyrene Petri dish, and left to cure under ambient conditions for 1 week. The film thickness produced was ~ 0.9 mm. For producing thinner films, the above mixtures were spread out on glass substrates by means of the Doctor Blade method.

Sylgard™ 184 sheets were prepared by mixing the polymer base with the curing agent in a (10:1) mass ratio. About 5 g of the mixture was poured into a 9 cm diameter polystyrene Petri dish, and left to cure at ambient conditions for 1 week. Capsaicin was then forced into the Sylgard™ 184 elastomer network by swelling the precured elastomer in 1 wt% capsaicin/benzene solution for two days. The elastomer was again dried for two days under ambient conditions and the deposits on the surface were removed by placing and peeling away a piece of scotch tape.

To determine the amount of capsaicin entrapped into Sylgard™ 184 elastomer, the samples were extensively extracted in acetonitrile using a soxhlet extractor for 24 hours. The acetonitrile and extracted materials with a total volume of ~ 200 mL were collected, and the solution was concentrated inside the air hood, under ambient conditions, to a volume of 75 mL. Then, 3 mL of the concentrated solution was thoroughly mixed with an equal volume of deionised (DI) water, and the concentration of capsaicin in the new solution was determined using high performance liquid chromatography (HPLC). The HPLC-determined concentration of capsaicin in this new 3 mL acetonitrile was used by simple material balance on capsaicin to calculate the total amount of capsaicin in the original 75 mL acetonitrile. It was then divided by the total mass (5 g) of the original sheet of Sylgard™ 184 in order to calculate the concentration of capsaicin entrapped into Sylgard™ 184 elastomer by the swelling method.

For standard capsaicin solutions, prepared from the compound obtained *via* Sigma-Aldrich, two main peaks at retention times of 13.1 min and 18.8 min, corresponding to capsaicin and dihydrocapsaicin, respectively[25] have been reported. These peaks were compared for each solution to determine its capsaicin content.

Coatings Characterisation

Variations in the morphology of capsaicin incorporated RTV11 and Sylgard™ 184 films were examined using an optical microscope (Model IX-70, Olympus) and with the non contact mode scanning probe microscopy (SPM) (Metrology 2000 from Molecular Imaging, using a Si_3N_4 cantilever with a spring constant of 21 – 78 N/m). All the SPM images presented in this study have a scan size of 80 μm × 80 μm and obtained with a scan rate of 0.20 Hz.

Coating surface wettability was evaluated in terms of water contact angle. Contact angle measurements were conducted using the contact angle goniometer video system with DI water as the probe liquid. Both dynamics and static contact angles were measured *via* the sessile drop method. For dynamic angles, the advancing and receding angles were achieved by the addition and removal, of water from the drops formed on the coating surface. For static angles, the water drop was placed on the coating surface and let to equilibrate without external force. Images of the drops were captured using the Dazzle DVC (Digital Video Creator). Its software and data were processed using the Scion Image Software.

Elastic modulus measurements for RTV11 and 1 wt% capsaicin blended RTV11 samples were conducted using the stress-strain method. In that, a small rectangular sheet (length ~ 25 mm, width ~ 6 mm, and thickness ~ 1 mm) of coating was vertically hung in air, its elongation under a particular weight was measured from the magnified images captured using the goniometer video system and the Dazzle DVC and its software. Stress [weight/(width × thickness)] was varied gradually up to ~ 0.13 MPa. For Sylgard™ 184, the method and results of determining its elastic modulus were reported elsewhere[26].

Leaching of Capsaicin from Capsaicin Incorporated RTV11

A 6.55 g sheet (~ 0.08 cm × 64 cm^2) of RTV11 with 1 wt% capsaicin bulk entrapped was immersed in a large glass beaker containing 500 mL DI water to study the leaching rate of capsaicin into water. The temperature of the water was room

temperature (23ºC). Water samples were collected at different time intervals up to one month. At each time interval, the water bath was stirred for 10 min, then 30 mL of the bath was extracted, subsequently 30 mL of fresh DI water was added to the bath which was stirred again for 10 minutes. Each extracted water sample was added with an equal volume of pure acetoniltrile and then the new solution was subjected to HPLC analysis.

For all HPLC (Model LC-10AT from Shimadzu with the symmetry C-18L column from Walters) analysis, identical procedures were followed. A mixture of acetonitrile + DI water (50:50 vol/vol) with a pH value of 2.1 was used as the mobile phase and 10 μL of the solution, of unknown capsaicin concentration, was injected into the column and flowed at a constant rate of 1 mL/min. In order to obtain the calibration curve, a set of standard solutions with concentration in the range of 13 – 5000 p.p.m. of the purchased capsaicin was prepared using the same mobile phase as the solvent.

Bacterial Attachment Study

The antifouling performance of the capsaicin treated silicone coatings would be better assessed by using the common fouling organisms, such as algae, tubeworms and diatoms. However, we had no access to such facility while the study was conducted. Nevertheless, it has been indicated that bacterial attachment and subsequent biofilm formation, in general, facilitate and enhance the attachment of macro fouling organisms. Also, as shown in the introduction section, capsaicin has demonstrated the effectiveness against the attachment of both micro fouler and macro fouler organisms. Therefore, we were only able to assess the coating's antibacterial performance by conducting bacterial attachment study in fresh water containing *Pseudomonas putida* or the enriched bacteria isolated from Lake Erie.

The detailed procedure for culturing the bacteria was described elsewhere[15,16,27]. Capsaicin treated and untreated silicone coatings were placed in 120 mL amber bottles, each containing 60–70 mL of the water having a particular type of bacteria. For some sets of the coating samples, one capsaicin treated coating and one capsaicin free coating were immersed in the same bottle. For another sets of the coating samples, capsaicin free coatings were immersed separately from capsaicin treated coatings. Care was taken to ensure all the coatings were arranged facing the bottom of the bottles to avoid the settlement of foreign species and organic matter. Coatings were observed at periodic intervals up to one month. At each time interval, a coating was removed, dipped gently in fresh DI water several times to remove loosely attached objects, and after drying off the DI water, they were immediately examined *via* an optical microscope.

RESULTS AND DISCUSSIONS

Miscibility of Capsaicin in Silicones

It is believed that the miscibility of capsaicin with the silicone matrix plays an important role for its distribution within the silicone coatings and consequently on its leaching. First, we attempted to experimentally evaluate the morphology of capsaicin when it was blended into the silicone coating. Sylgard™ 184, a transparent silicone, allows materials entrapped to be observed by optical microscope. Therefore, to roughly examine the miscibility of capsaicin with silicones, we blended capsaicin with Sylgard™ 184 base using toluene as the common solvent and the mixtures were kept inside the air hood for four days to dry off the solvent at room temperature. As shown in *Figure 1*, the resulting coating

showed the formation of large capsaicin aggregates/crystals inside silicone matrix. The size of the aggregates was analysed by an image analysis software and estimated to be in the range of 14-33 μm.

The miscibility of a substance (1) with a polymer (2) can be roughly predicted by the substance polymer interaction parameter, χ_{12}. According to the Flory-Huggins theory, χ_{12} is given by *Equation 1*:

$$\chi_{12} = (V_1/RT) (\delta_1 - \delta_2)^2 \quad \ldots 1$$

where V_1 is the molar volume of the smaller species, capsaicin in our case, R and T are respectively the ideal gas constant and the temperature, and δ_1 and δ_2 are respectively the solubility parameters of capsaicin and the polymer. A smaller χ_{12} indicates a higher chance that the system would be miscible and a value of $\chi_{12} < 0.5$ is the Flory-Huggins criterion for a solvent/polymer system to be completely miscible. For PDMS, we used the literature value of its solubility parameter; 14.9 $MPa^{1/2}$[28]. For capsaicin, we predicted its solubility parameter by the group contribution method, according to the relation [$\delta = (\sum F_i) / (M/\rho)$], where F_i is the molar attraction constant of group i in capsaicin structure, and M and ρ are respectively the molecular weight (305.4 g/mol) and density (1.15 g/cm^3) of capsaicin. Two sets of F_is were used, *i.e.* Hoy's and van Krevelen's, both found in van Krevelen[29] and the solubility parameter of capsaicin was 22.44 $MPa^{1/2}$ and 25.77 $MPa^{1/2}$ by applying Hoy's and van Krevelen's data, respectively. Using the average of the two estimated solubility parameters of capsaicin into *Equation 1*, the χ_{12} value for capsaicin/PDMS system was estimated to be 9.092, indicating that capsaicin was immiscible with PDMS. Therefore, even when capsaicin was mixed into the silicone using a common miscible solvent (toluene), it phase separated from silicone upon removal of the solvent and resulted in the formation of large capsaicin aggregates/crystals.

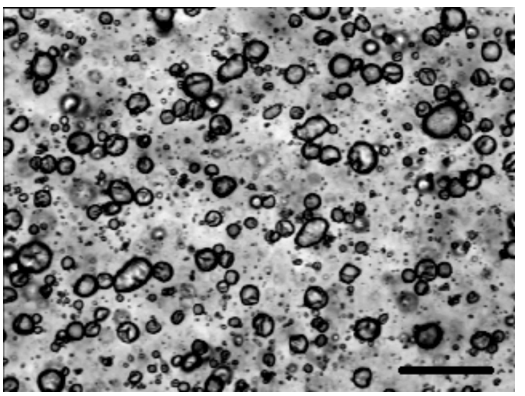

Figure 1. Optical microscope (transmission bright field) image of resulting capsaicin distribution in the bulk of Sylgard™ 184 base material (without curing agent). Toluene was used as the common solvent to mix capsaicin with Sylgard™ 184. The image size is (570 × 480) μm. The scale bar shown in the image is 100 μm.

Entrapping Capsaicin into Sylgard™ 184 by the Swelling Method

Previous works[24] have also shown that direct blending of capsaicin and Sylgard™184 resulted in uncured coating. Sylgard™ 184 is crosslinked *via* a hydrosilylation-type reaction catalysed by a Pt-based catalyst. It is known that Pt-based catalysts could be easily poisoned by trace amounts of certain compounds[30], including amide. Capsaicin, which contains an amide group, likely poisoned the Pt-based catalyst and inhibited the curing of Sylgard™ 184. Therefore, we attempted to utilise a swelling method, in which capsaicin molecules were forced into the bulk of the precured Sylgard™ 184 elastomer during the process of swelling in a capsaicin solution (*e.g.* capsaicin/toluene). Since the size of capsaicin molecule was comparable to that of

some solvents (*e.g*. toluene) that swell silicone elastomer, capsaicin molecules could seep into the silicone elastomer network along with solvent molecules while the swelling takes place. Then, upon removal of the low volatile solvent, the coating returns to its original volumes with non volatile capsaicin molecules entrapped. The amount of capsaicin entrapped into Sylgard^{TM} 184 by the swelling method (with toluene as the solvent) was determined to be 0.37 wt% capsaicin in the coating.

Coating Properties Variation of Capsaicin-incorporated RTV11

It is known that tin-based catalyst is much more resistant to poisoning than the Pt-based catalyst[30]. Thus, RTV11, which has a tin-based catalyst, was chosen as the second coating carrier for directly blended with capsaicin. It was observed that the capsaicin blended RTV11 coatings were cured similarly as the capsaicin free RTV11 coatings.

The contact angles for RTV11 films containing various concentrations of capsaicin (0.1 – 1 wt%) were measured. RTV11 surfaces without capsaicin had advancing, static and receding contact angles of 103º, 100º and 95º, respectively. The advancing and static contact angles were almost unaffected by the addition of capsaicin. The receding contact angles decreased slightly as capsaicin concentration increased, a value of 87º for 1 wt% capsaicin was observed and this could be because of a slight increase in the surface heterogeneity due to the existence of some capsaicin aggregates in the sub layer close to the surface. The indifference in the advancing and static contact angles between both controlled RTV11 and capsaicin incorporated RTV11 samples suggested that most capsaicin molecules entrapped inside the bulk of the polymer matrix rather than aggregated to the surface. Otherwise, the advancing and the static contact angle is expected to drop due to the fact that capsaicin has a higher surface energy (~ 45 mJ/m^2) than PDMS (~ 20-24 mJ/m^2). The surface energy of capsaicin was predicted here by the group contribution method following the procedures of van Krevelen[29]. Moreover, as measured by scanning probe microscopy (SPM), the addition of capsaicin only slightly increased the surface roughness of RTV11. The surface roughness (R_q) for RTV11 film (*Figure 2a*) and 1 wt% capsaicin blended RTV11 film (*Figure 2b*) were 7 nm and 12 nm, respectively.

The elastic modulus of the films of RTV11, and RTV11 containing 1 wt% capsaicin were measured and found to be 1.56 MPa and 1.57 MPa, respectively. The value is consistent with that reported for RTV11[31]. The indifference in the elastic modulus for the capsaicin free-RTV11 and capsaicin-blended RTV11 could indicate that the low content of capsaicin (up to 1 wt%) were insignificant in affecting the curing behaviours and bulk properties of RTV11. The elastic modulus was expected to drop significantly for the uncured coating.

Leaching of Capsaicin from RTV11 into Water

The capsaicin molecules incorporated into the bulk of a coating should leach out in order for them to antifoul, thus some degree of water solubility of capsaicin is necessary. From literature[32], the solubility of capsaicin in water is measured experimentally at room conditions and found to be 60 mg/L.

The capsaicin entrapped RTV11 coatings were subjected to leaching studies in static cells. As shown in *Figure 3*, capsaicin leached out rapidly from RTV11 within the first seven days, and then slowed down as time proceeded. The cumulative mass leached out after the first and fourth weeks were about 159 and

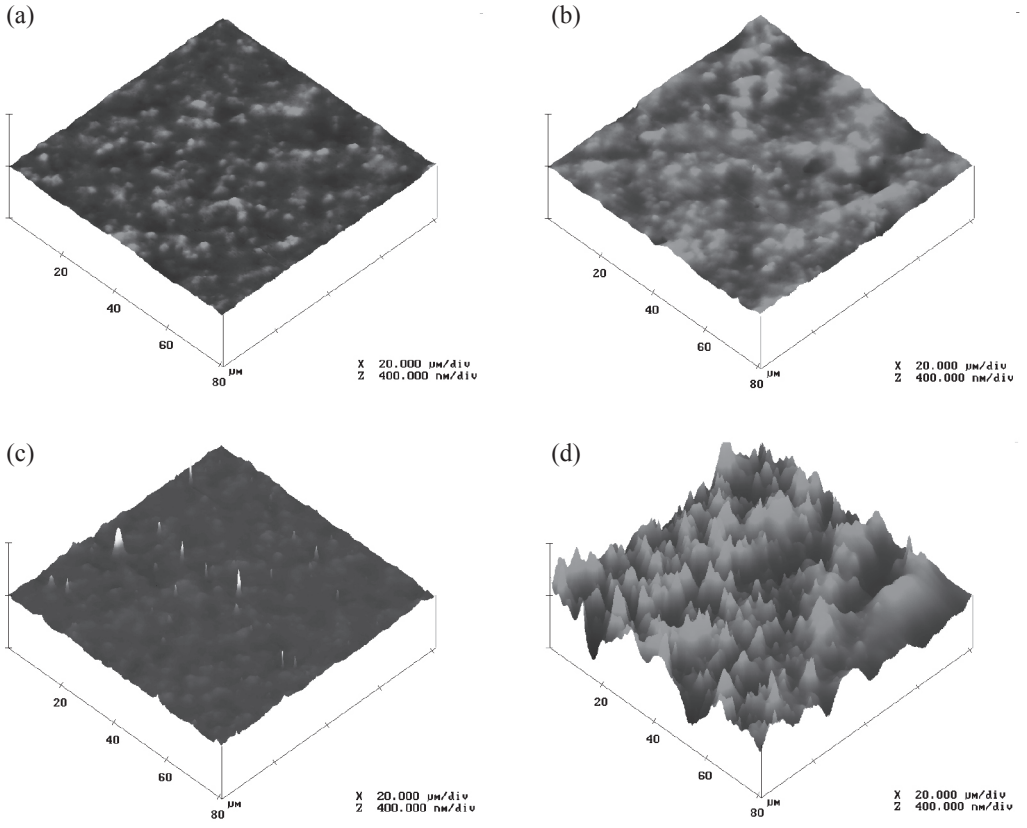

Figure 2. Surface topographies (size: 80 μm × 80 μm in the horizontal xy plane; z-scale: 400 nm in the vertical z axis) of (a) Controlled RTV11 film (b) RTV11 film containing 1 wt% capsaicin (c) RTV11 film after 14 days of immersion in DI water (d) RTV11 film containing 1 wt% capsaicin after 14 days of immersion in DI water. The root mean square (RMS) surface roughness for the coatings shown in (a), (b), (c), and (d) were 6.7, 12.3, 10.5, and 88.0 nm, respectively. The images were generated using scanning probe microscopy with the non contact mode at a scan rate of 0.20 Hz.

201 μg/cm^2, respectively. Approximately 38% of capsaicin original mass has leached after one month of immersion. By extrapolation, it will take approximately eight months for capsaicin to leach out completely.

The relatively high leaching of capsaicin from RTV11 could be due to capsaicin being highly immiscible in silicones as discussed. Partial degradation and erosion of the RTV11 matrix in water, which has been confirmed experimentally[33] could contribute and facilitate the leaching. Since RTV11 has a high content of inorganic fillers (32 wt% $CaCO_3$), it could lead to presence of voids in between the filler particles and at the filler/polymer interface allowing water molecules to seep into the silicone matrix through these empty spaces and carry the dissolved capsaicin molecules with them as they leave the coating. It could be

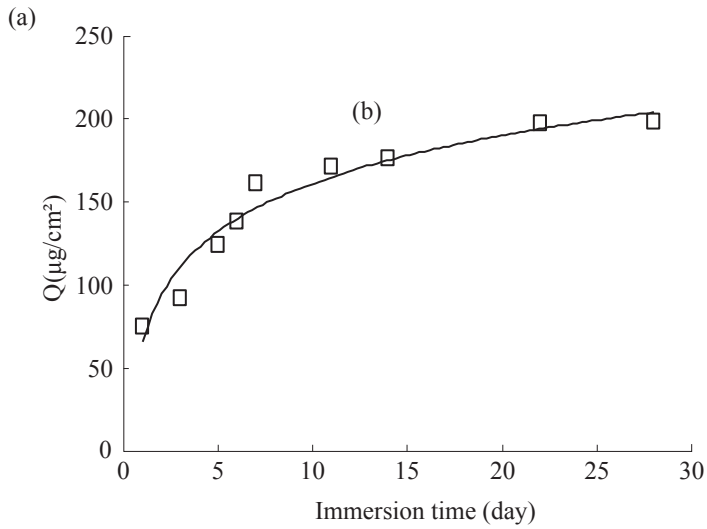

Figure 3. Capsaicin cumulative mass per area (Q, in μg/cm^2) released from 1 wt% capsaicin incorporated RTV11 sheet (total mass and surface area of the sheet were respectively 6.55 g and 114 cm^2), plotted against time of immersion in DI water. Toluene was used as the common solvent to mix capsaicin with RTV11. Solid line is used to show the trend.

the large crystals/aggregates formed inside the bulk of the coating matrix, that contributed to the fast leaching, which was also observed for another compound, benzoic acid, incorporated into Sylgard™ 184[26].

In this study, only capsaicin leaching from RTV11 matrix was measured and reported. However, capsaicin leaching from Sylgard™ 184 matrix would be expected to be less compared to RTV11 due to the initial loading of capsaicin in Sylgard™ 184 matrix which was less (0.37 wt%) than the RTV11 (1 wt%). Sylgard™ 184 matrix did not contain fillers which would make the polymer chains more compact, while RTV11 matrix was filled with high content of inorganic filler (32 wt% $CaCO_3$) which would generate some inner voids thus, making the water molecules easier to diffuse. These arguments were supported by similar studies in our laboratory, where the leaching of different antifoulants (sodium benzoate[26], benzoic acid[26], zosteric acid[27,34] and tannic acid[35]) were measured from Sylgard™ 184 matrix and RTV11 matrix into water at room conditions. Both studies confirmed that the leaching of the antifoulants from Sylgard™ 184 matrix was always less compared to RTV11 matrix.

Effect of Immersion in Water on Coating's Surface and Bulk Properties

The contact angle data for RTV11 films were taken for different intervals up to 14 days of immersion in water. The advancing contact angle almost remained constant at the respective value of controlled as prepared RTV11 films. The receding contact angles, however, showed a gradual decrease down to a value of 80º at the end of 14 days. Consequently, the contact angles hysteresis (difference between the advancing and receding angles) increased from 8° initially to 23º after 14 days of immersion, possibly

due to slow surface erosion, which resulted in an increase in surface roughness. The increase in surface roughness was verified by SPM scans. The room mean square roughness, R_q, for an 80 μm × 80 μm area increased from ~ 7 nm for as prepared RTV11 films (*Figure 2a*) to ~ 10 nm for 14 day water-aged RTV11 films (*Figure 2c*). The bulk modulus, however, only decreased slightly (from 1.56 MPa to 1.37 MPa after 42 days of immersion), thus it would have insignificant contribution to the difference in bacterial attachment.

For 1 wt% capsaicin blended RTV11 coatings immersed in water for 14 days, the advancing contact angles increased to a value of 109º, whereas the receding contact angle decreased to a value of 79º. The increase in the contact angles hysteresis (to 30º) could likely be the result of an increase in surface roughness. SPM scans revealed that R_q, for an 80 μm × 80 μm area, did increase considerably from ~ 12 nm for as prepared films (*Figure 2(b)*) to ~ 88 nm after 14 days of immersion (*Figure 2d*). The following scenario could be used to explain the observation in surface roughness. The blending of capsaicin with RTV11 using a common solvent resulted in various sized capsaicin aggregates/crystals inside the coating matrix. Once immersed in water, it was possible that most of capsaicin aggregates that had direct contact with the bulk of water could be dissolved and leached out quickly, leaving behind various sized holes that contributed to the irregular surface topography and an increase in the surface roughness.

Bacterial Attachment Study of Capsaicin Treated Silicones

Some representative bacterial attachment images are presented in *Figures 4* and *5*. Fewer bacteria were attached to the capsaicin entrapped Sylgard™ 184 coatings (*Figure 4a*) as compared to the Sylgard™ 184 coatings alone (*Figure 4b*). Similarly, much less bacteria were attached to capsaicin blended RTV11 coating (*Figure 5a*) as compared to RTV11 coating alone (*Figure 5b*). Comparing the capsaicin free coatings, it was observed that RTV11 (*Figure 5b*) had a higher tendency for biofilm formation than that of Sylgard™ 184 (*Figure 4b*), which could be attributed to the fact that RTV11 has slightly higher bulk modulus and surface roughness than those of Sylgard™ 184. Nevertheless, the clear reduction in bacterial population on the capsaicin treated coating surface, especially capsaicin RTV11 coatings, suggested that capsaicin can effectively inhibit the attachment of bacteria tested. However, the antibacterial effectiveness of capsaicin treated silicones is likely short lived due to the rapid leaching of capsaicin coupled with the dramatic increases in surface roughness of the coatings immersed in water.

CONCLUSIONS

Capsaicin was incorporated into two silicone coatings, Sylgard™ 184 and RTV11. For Sylgard™ 184, the entrapment was achieved by forcing capsaicin molecules into a silicone network through the swelling of the elastomer in a capsaicin/toluene solution. Simple blending of capsaicin with the uncured Sylgard™ 184 mixture resulted in the poisoning of Pt-based catalyst and unsuccessful curing of the coating. Due to the highly immiscible nature of capsaicin/silicone, the maximum amount of capsaicin that could be entrapped in Sylgard™ 184 by the swelling technique was found to be 0.37 wt% of the coating. For capsaicin-RTV11 coatings, the entrapment was achieved by blending capsaicin with RTV11 base elastomer using toluene as a common solvent. The small amounts (up to 1 wt.%) of capsaicin incorporated in the

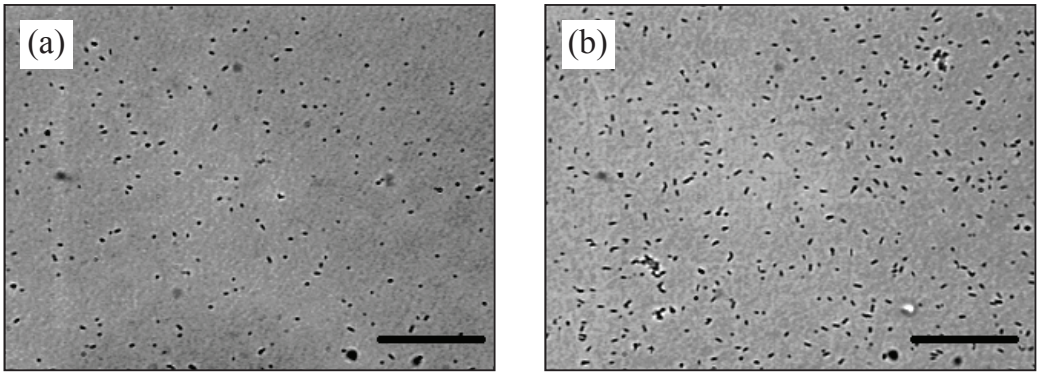

Figure 4. Optical microscopic (transmission bright field) images of (a) Capsaicin entrapped Sylgard™ 184 and (b) Control Sylgard™ 184 coatings after immersing in water containing P. putida *bacteria for 10 days. The size for both images is (190 × 144) μm. The images correspond to the set of samples in which one sample of capsaicin treated Sylgard™ 184 and one sample of capsaicin free Sylgard™ 184 coatings were both immersed in the same bottle where the bacteria were subjected to the same environment and provided with two surfaces to choose. The scale bar shown in both images is 40 μm.*

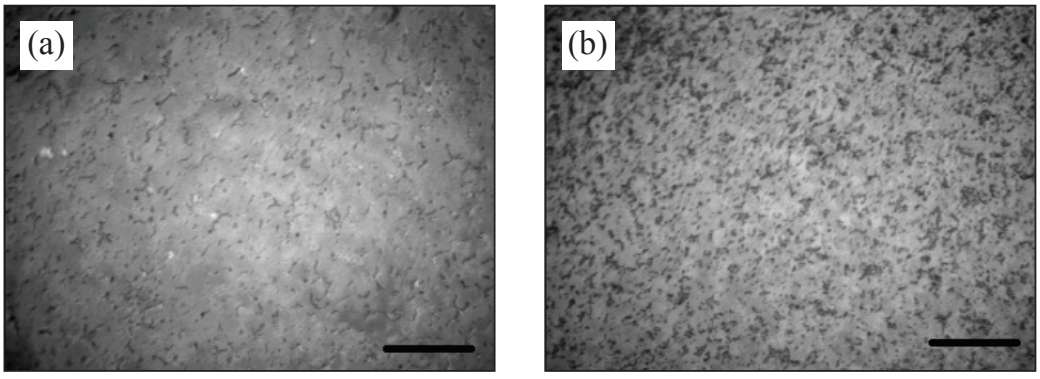

Figure 5. Optical microscopic (reflection bright field) images of bacterial attachment on RTV11 coatings having (a) 1 wt% capsaicin and (b) No capsaicin after the coatings have been immersed in water containing Lake Erie bacteria for 14 days. The size for both images is (285 × 215) μm. The images correspond to the set of samples in which one sample of capsaicin treated RTV11 and one sample of capsaicin free RTV11 coatings were both immersed in the same bottle where the bacteria were subjected to the same environment and provided with two surfaces to choose. The scale bar shown in both images is 50 μm.

silicone coatings had insignificant effect on the surface and bulk properties of the coatings, suggesting that the unique easy release properties of the silicone coatings could be maintained. For a short period of time (up to 14 days), both capsaicin incorporated silicone coatings exhibited enhancement in antifouling as compared to silicone coatings alone. However, the antifouling longevity of the coatings was hampered due to the fast leaching of capsaicin and the consequent increase in surface roughness of the coating upon water immersion. The fast leaching of capsaicin could be attributed by the large aggregates/crystals formed in the coating matrix *i.e.* RTV11 upon evaporation of the solvent used for incorporation.

ACKNOWLEDGEMENT

We are grateful for the financial support from the Ohio Sea Grant (Project: R/MB-2) and Ohio Board of Regents (R5905-OBR). We thank Mr. S-H. Choi for performing SPM scans, Dr. T. Cutright and Mr. Q. W. Xu for assisting in the bacterial attachment studies. Abdulhadi Al-Juhani is also very thankful to King Fahd University of Petroleum & Minerals (KFUPM), Saudi Arabia, for providing him a full scholarship and financial support throughout the project and his entire PhD study.

Date of receipt: June 2014
Date of acceptance: August 2014

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