# Novel Phase Change Material Icephobic Coating for Ice Mitigation in Marine Environments

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**Abstract:** Novel ice-phobic coatings were developed that employ organophosphorous phase change materials (PCMs). PCMs exist in a passive or dormant state under most environmental conditions, but PCMs undergo solid-solid phase changes over a narrow temperature range slightly below at which ice formation occurs. As ice forms on the surface, some of the latent heat of freezing passes to PCMs. This heat is absorbed by the PCMs and causes local strain on the coating surface and results in removal of the ice. Minimal force (<1psi) is required to remove ice from test surfaces treated with PCM ice-phobic coating technology.

**Key words:** Icephobic, anti-icing, de-icing, marine coating

## 1. INTRODUCTION

Ice build-up is a serious concern for industries such as aerospace, maritime, power transmission, telecommunication, and ground transportation with far reaching economic and safety impacts. Icing also reduces military preparedness and rescue response in times of emergency. Icing reduces ship stability, adversely affects aerodynamic performance of aircraft, and disrupts vital communication signals. The effects of icing are not limited solely to damage to machinery and equipment, but also cause injury and loss of life. Conventional methods for controlling icing are limited to toxic deicing fluids, sacrificial coatings that need to be frequently reapplied, or removal by costly thermal and mechanical systems.

The adhesion of ice to structures, e.g. naval and fishing vessels, ice breakers, communication and radar equipment, etc., can have serious safety consequences [1]. Currently, the removal of ice build up on shipboard structures is done through the use of deicing materials and the use of brute force by means of baseball bats, mallets, shovels and heat guns. De-icing materials such as ethylene glycol, calcium chloride and urea are in use but have drawbacks such as limited temperature use and unwanted side effects (irritation with skin, harmful dust, corrosive to metals, and creation of slippery surfaces) [2]. This research demonstrates the feasibility of designing a surface that stresses the ice-surface interface as the ice forms without interfering with normal shipboard operating procedures. A novel coating containing phase change materials (PCMs) encapsulated within a flexible, film-forming hydrophobic polymer was developed.

PCM based ice-phobic coatings use a combination of low surface energy materials with heat driven motions of the surface coating to inhibit ice attachment on surfaces. Prior efforts by other researchers have relied entirely on low surface energy materials [3,4,5]. Like previous approaches, PCM-based coatings yield low surface energy films that minimize ice accretion. Unlike other approaches to the icing problem, the proposed experimental coating relies on the thermodynamic properties of the PCM. When a PCM-based coating is cooled below 0°C, adjacent regions within the polymer coating expand and contract due to the solid-solid phase changes, stressing the ice-coating interface. Stressing at the ice-PCM coating interface effectively de-ices the surface observed by the ice detaching, or by reducing the force required to remove ice. A depiction of PCM icephobic coating technology is presented in Figure 1.

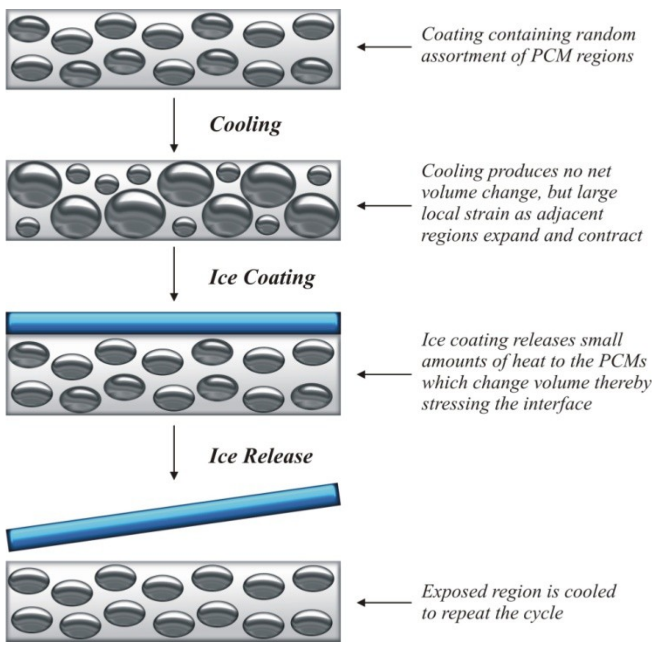



**Figure 1.** Schematic representation of the PCM de-icing

What happens during icing events is illustrated in Figure 1. The steps that lead to the cycle for mechanical rejection of ice are: 1) Micro-phase PCM regions near the coating surface undergo *solid-solid* phase changes over a narrow temperature range, slightly below where ice formation occurs. Cooling below $0^{o}C$ by the air flow results in local contraction of the polysiloxane carrier resin and simultaneous expansion or stretching of the PCM such that the composite bulk film, on the average, contracts relatively little if at all. 2) Super-cooled water droplets coat the coating surface and freeze. As ice forms on the surface, some of the latent heat of freezing of ice passes to these PCMs near the surface. 3) This heat is absorbed by the PCMs and causes solid-solid phase changes. Surface regions of the coating expand and adjacent regions contract. Uniform distribution of micro-spherical PCMs facilitates this process. The ice-coating interface experiences local shear stress of alternating sign. This causes local failure of the ice-coating bond, and de-icing. The actual lateral local displacements of the surface are on the order of one tenth the diameter of the particles. These displacements produce a local linear strain parallel to the coating surface of about 0.1, more than enough to locally break the ice-surface bond.

## 2. PHASE CHANGE TEMPERATURE DETERMINATION BY DSC

The temperature range where phase change occurs in PCM-base coatings was determined by differential scanning calorimetry (DSC). DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. DSC is used in studying phase transitions involving energy or heat capacity changes. By measuring the difference in heat flow between the sample and reference, differential scanning calorimeters measure the amount of heat absorbed or released during these transitions. Two scans were performed per sample cooling to -40°C and heating to 60°C. Films of fully formulated coatings were used for testing. Results from DSC show that PCM-based coatings undergo phase change from -11 to -5°C. Peak adsorption was observed at -5°C. The broad transitions observed (Figure 2) overall are suggestive of polymeric or complex mixture systems.

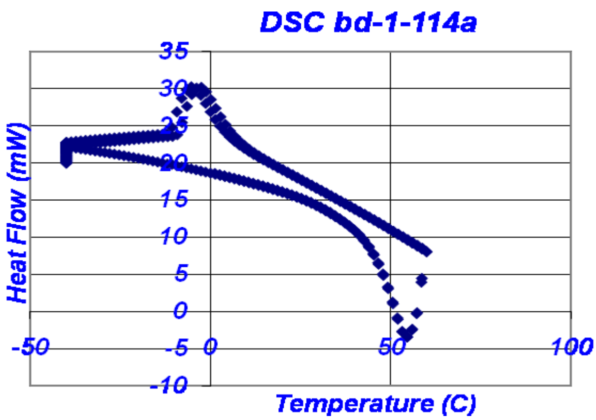



**Figure 2.** Phase change temperature determination by DSC

# 3. CRYO-CLEAVE SEM IMAGING OF PCM -BASED ICEPHOBIC COATING

PCM size and dispersion in polymeric matrix was imaged by Cryo-cleave SEM imaging. In Cryo-cleave SEM, images can be made of the fracture surfaces below the coating surface (side view). The PCM-based coating applied to an aluminum panel was rapidly frozen in liquid nitrogen. The cryo-chamber is equipped with a knife that can be handled from outside by means of a level to fracture the sample for applications in which imaging of the surface of inner structures is aimed. Imaging from Cryo-cleave SEM (10,000XMagnification) is presented in Figures 3. The image shows that PCMs uniformly dispersed in the coating matrix as 2-3µm diameter spheres.

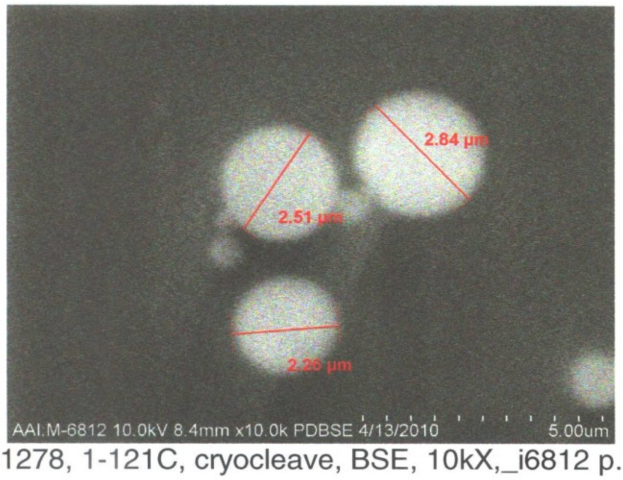



**Figure 3.** SEM Image of PCM 3000 (formula 1-121C), 10kX magnification

# 4. ICE-ADHESION TESTING

Ice adhesion testing by double lapshear pull tests (ASTM D3528) and by Centrifuge Ice Adhesion Test (CAT) demonstrate de-icing properties of PCM-based coatings. Ice adhesion testing following ASTM (2002) D3528-96 was developed by the US Army Corps of Engineers CRREL in Hanover, NH. The Centrifuge Ice Adhesion Test (CAT) was developed at the Anti-Icing Materials International Laboratory (AMIL) of the University of Quebec at Chicoutimi.

## *4.1 Ice-adhesion Testing by Double Lap Shear (ASTM D3528-96)*

Ice adhesion testing by double lapshear involved the removal of aluminum test coupons coated with candidate PCM-based icephobic coatings from an iced test fixture. This test method was employed to qualify PCM chemistries as icephobic.

Aluminum (3.175mm thick, 2024) test coupons, 25.4mm wide by 101.5mm long, with a hole drilled in the top are used for testing. Three coupons are coated with each prospective formulation. Each sample coupon is coated with the material to be tested and then placed into the groove in the test fixture. It is held centered by a small groove in the bottom of the base piece. The top is held centered by a wrap of tape which also forms a watertight seal around the coupon. The space between the coupon and base piece is filled with de-ionized and de-gassed water and frozen at -10$^0$C. The test fixture is mounted in a United Test Systems UTM, model # SFM-50kN with environmental chamber and Datum 3.0 analytical data acquisition software is used for conducting the test. The chamber is connected to a LN2 cryogenic tank to maintain sub-zero temperatures in the chamber. The test is conducted at -4$^0$C, and the force required to pull the sample coupon out of ice measured. The test coupon is pulled at a rate of 0.127mm/min for the first 10 minutes and then at a rate of 12.7mn/min until a total distance of 25.4mm is reached.

Ice adhesion to hundreds of prospective PCM-based coatings was measured following ASTM D D3528 in attempts to optimize de-icing properties of PCM coating chemistry. Results are summarized in Figure 4. Minimal force is required to remove test coupons coated with the optimized PCM-based coating, less than 1psi (5.5±3.9 kPa). By contrast, the force required to remove ice from polyurethane (MIL-PRF-85285D) coated test surfaces is 324.1±35.3 kPa.

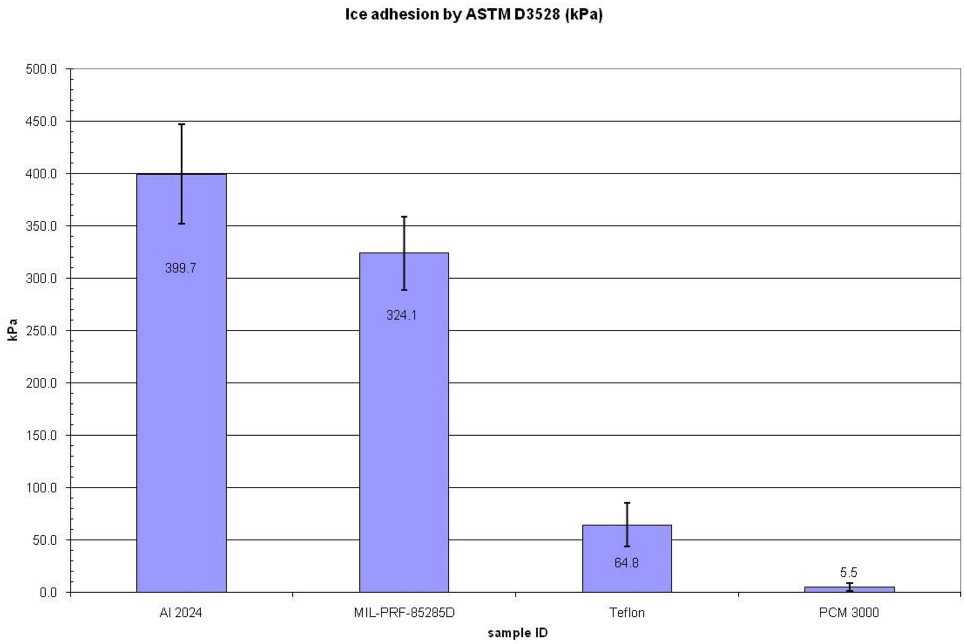



**Figure 4.** Double lap shear test fixtures

### *4.2 Ice Adhesion by Centrifuge Ice Adhesion Test (CAT)*

Testing at AMIL was performed to measure the adhesion reduction of candidate ice-phobic coatings compared to uncoated (control) surfaces. Aluminum beams are iced in a cold room and then ice adhesion tested as a function of centrifugal force (F). The test beam dimensions are shown in Figure 5.

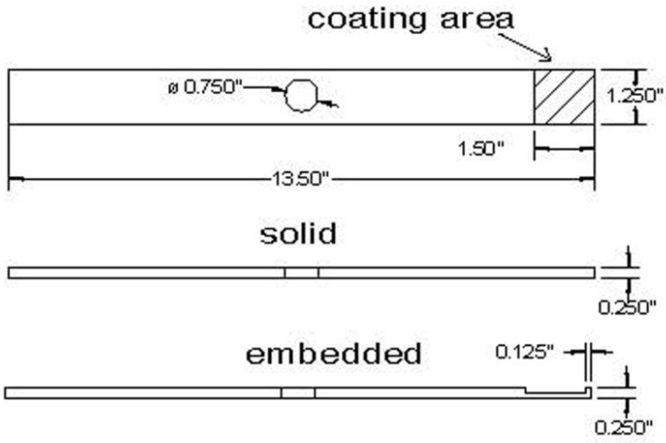



**Figure 5.** Test Beam Dimensions

The beam is rotated at an accelerated speed until ice detaches due to centrifugal force. Sensors detect ice detachment in real time and the time to detachment and rotation speed recorded. Three aluminum beams were coated with the PCM-based formula optimized through ice adhesion by double lapshear testing, PCM 3000. PCM 3000 was sprayed to a masked area ($12cm^2$) on one end of the solid bar. The coating was cured 48 hours at 25°C, the masking removed, and test surfaces shipped to AMIL. Ice was frozen to the test surfaces in 32 minutes at -8.0±0.1°C. The test was conducted at -10.0±0.1°C. Bare aluminum bars were used as controls.

Results from CAT testing at AMIL confirm that PCM 3000 is icephobic. AMIL reported an Adhesion Reduction Factor (ARF) of 39.0 for PCM 3000. The ARF is calculated by comparing average shear stress to remove ice by centrifugal force measured using three coated aluminum test surfaces to the average stress measured on three bare aluminum controls, the higher the ARF, the more ice-phobic the coating. The ARF of Teflon is roughly 7.0. Only sacrificial coatings, such as lithium and silicone greases, achieve greater than 30.0. Based on results from AMIL, ice shedding properties of PCM-based ice-phobic coatings exceed that of all other commercially available products. PCM-based ice-phobic coatings yield a durable more permanent solution to the icing problem than soft silicone or grease-based sacrificial coatings.

## 5. ICE ACCRETION TESTING

PCM-based coatings and controls were weathered for about six months outside research facilities in East Falmouth, MA. Steel and composite test panels were coated with MIL-P-24635 and over coated with PCM-based coating formulas. Test panels were fixed to test racks for a southerly facing exposure. Test panels were exposed to a total of 21.5 inches of precipitation during the test period between January 13 and June 27, 2006.

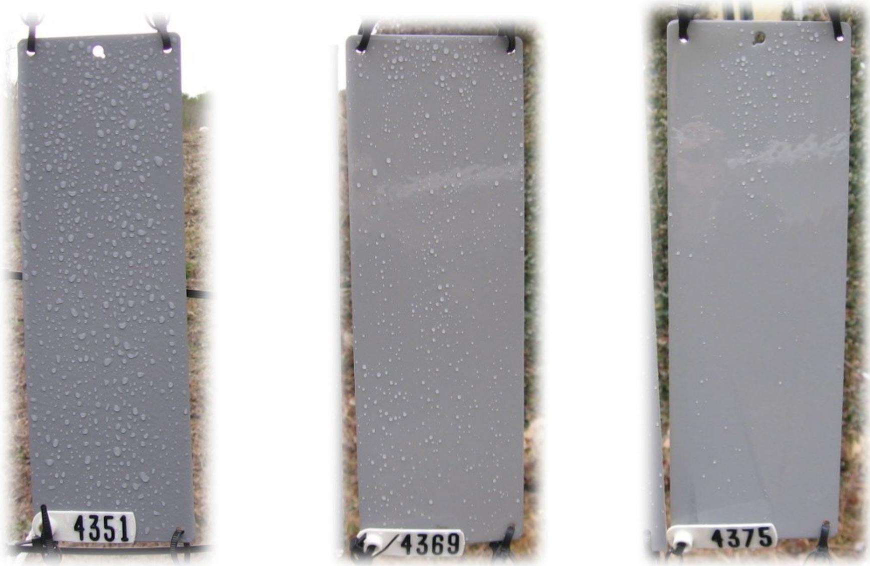
Test panels were monitored and documented after snow-ice events and using pictures and the aid of a computer graphics program, the formulations were then evaluated by measuring the average size and frequency of ice formation and giving it a rating. ASTM D714, *Standard Test Method for Evaluating Degree of Blistering of Paints*, has been modified for this test by substituting the size and frequency of paint blistering with the size and frequency ice bead formation. The results are rated based on their performance, bead size 10 being the best and 0 being the worst. The frequency of the beads is rated as none being the best case and dense being the worst. The results are presented in Table 1 and Figure 6. The type of substrate did not seem to have any influence on the rating results. For the most part, ice formation was the same for a given formulation, regardless of the underlying substrate.

**Table 1.** Vertical Angle Panel Outdoor Weather Testing Observations and Results

| Start Date: 1/13/06 | | Date: 1/23/06<br>Time: 8:00 am<br>Temp: 33°F<br>Condition: After rain-freeze event | | Date: 2/1/06<br>Time: 8:00 am<br>Temp: 32°F<br>Condition: After rain-freeze event | | Date: 2/13/06<br>Time: 10:00 am<br>Temp: 27°F<br>Condition: During snow event | |
|---|---|---|---|---|---|---|---|
| Formulation | Substrate Type | Ice Bead Size* | λ** | Ice Bead Size* | λ** | Ice Bead Size* | λ** |
| MIL-P-24635 Silicone-Alkyd Enamel Control | Steel | 4 | Medium-Dense | 4 | Medium-Dense | 10 | Dry |
| MIL-P-24635 Silicone-Alkyd Enamel Control | Alum 5052 | 4 | Medium-Dense | 4 | Medium-Dense | 10 | Dry |
| MIL-P-24635 Silicone-Alkyd Enamel Control | GFVE | 4 | Medium-Dense | 4 | Medium-Dense | 10 | Dry |
| 0% PCM, | Steel | 7 | Medium | 7 | Medium | 10 | Dry |
| 0% PCM | Alum 5052 | 7 | Medium | 7 | Medium | 10 | Dry |
| 0% PCM | GFVE | 7 | Medium | 7 | Medium | 10 | Dry |
| 10% PCM | Steel | 8 | Few | 7 | Few | 10 | Dry |
| 10% PCM | Alum 5052 | 8 | Few | 8 | Few | 10 | Dry |
| 10% PCM | GFVE | 8 | Few | 8 | Few | 10 | Dry |

* Ice Bead Size: Scale from 0-10 (0 = >12mm, 2 = 6mm, 4 = 3mm, 6 = 2mm, 8 = 1mm, 10 = 0mm)

** Frequency (ASTM D714): Dense (D), Medium Dense (MD), Medium (M), Few (F)




MIL-P-24635 Silicone-Alkyd Enamel Control | 0% PCM, Polysiloxane Carrier Resin | 10% PCM, Polysiloxane Carrier Resin

**Figure 6.** Vertical Angle Steel Substrate Test Panels After Rain-Freeze Event

## 6. DEMONSTRATION ON RADOME

The FAA has concluded icing on radar and communications equipment to be a serious hazard to people and equipment on the ground and detrimental to system performance. Ice normally does not de-bond from the radome structures until buildup is extremely heavy, ice masses exceeding 200lb in weight before de-bonding occurs. Ice thrown through the air at this weight and velocity is enough to kill or severely injure a person and damage equipment on the ground. The FAA has charged the Volpe National Transportation Systems Center (Cambridge, MA) with finding a solution to the icing problem.

Volpe Center engineers Mr. Thomas Seliga and Mr. Allen Mackey arranged a demonstration project to prove the efficacy of incorporating ePaint’s PCM-based ice-phobic coating technology onto radome and communication equipment. The demonstration project involved painting a candidate PCM-based formula onto a 20’ EASAT radome, placing the radome into service, and blasting the radome with snow and ice. This demonstration project was a cooperative effort between ePaint, The Volpe Center, Sensis Corp., and the FAA.

PCM-based ice-phobic coating was applied to an EASAT radome at Sensis Corporation facility in Syracuse, NY. On March 9, 2009, the radome was transferred and installed on a tower at Sensis Corp. testing facility located at Syracuse Hancock International Airport. The EASAT radome is 20’ long and operates by spinning one revolution per second. Radio frequency testing performed by Sensis Corp. determined there were no issues with the coating interfering with signal transmission or reception.

**Figure 7.** Application of PCM **Figure 8.** EASAT Radome

Testing commenced the morning of March 13, 2009. Temperature and relative humidity on the tower ranged from 26-30$^{o}$F during testing, humidity was low. According to Greek Peak Summit representative JR Hill, environmental conditions were perfect for making snow and ice. The ice-phobic painted radome was blasted with wet snow and ice from snow making equipment operated by Greek Peak Summit. The radome was blasted for approximately three hours with wet snow and ice, stopping periodically to evaluate effectiveness of the coating.

**Figure 9.** Blasting the EASAT Radome with Wet Snow and Ice

Within several minutes of resuming the operation of the radome and snow making equipment, a large section of ice shed and landed about 100' from the tower. The shed ice was about 12-20mm in thickness, released from the coating surface. Testing was continued for approximately another two hours and during that time, ice continued to shed off the radome structure at 5-10 minute intervals.

# 7. CONCLUSION

A novel ice-phobic coating was discovered that yields passive anti-icing and dynamic de-icing properties to prevent ice accretion on metallic and composite surfaces. The shear induced stress from local expansion-contraction regions results in stressing of the ice-coating interface. The research was significant as the coatings based on PCMs potentially offer more effective, less costly and more durable replacements for the existing icephobic coatings.

PCM-based icephobic coatings are transparent, flexible and offer a highly hydrophobic surface. Surfaces coated with PCM 3000 have high contact angles, so water just beads and runs off the surface. Ice accretion measurements showed very little ice accumulation on the surfaces coated with our icephobic coatings. Ice that does accumulated on these coating surfaces can be easily removed. Ice adhesion measurements indicate that minimal (<1psi) force is required to remove accreted ice.

# ACKNOWLEDGEMENTS

The authors wish to thank Dr. Roger Crane of the Naval Surface Warfare Center (Carderock), and Dr. Elisabeth Berman of AFRL/MLSC (Wright-Patterson AFB), program managers for SBIR Contracts N00167-05-C-0026 and FA 8650-08-C-5601 respectively.

The authors acknowledge the efforts of Volpe Center engineers Mr. Thomas Seliga and Mr. Allen Mackey to arrange and oversee the demonstration project on a radome operating at the Syracuse International Airport (Syracuse, NY).

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