DEICING SILICONE COATING BASED ON BIDIRECTIONAL MIGRATION EFFECT OF ALKANE MOLECULES

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General Introduction

Among various deicing methods, deicing coating is a convenient and effective one in preventing ice accumulation on the protected surfaces [1, 2]. In this study, we demonstrated a novel deicing coating based on the bidirectional migration effect of alkane molecules added to the silicone coating. When the environmental temperature decreases to its freezing point, the alkane molecule migrates to the silicone coating surface via phase separation process, forming hydrophobic alkane films that help to decrease nucleation and adhesion of water droplets. Interestingly, the alkane molecule can melt and come back into the silicone matrix when the environmental temperature is above its melting point. This would favor to prolong the service life of the novel deicing coating. In this study this phenomenon is termed "bidirectional migration" so as to emphasize the feature that the alkane molecule can *diffuse out of* or *come back into* the silicone matrix under the influence of environmental temperature.

Experimental

The silicone pre-polymer, curing agent and two kinds of the alkane molecules were commercially available. The weight ratio of silicone pre-polymer to curing agent was 10:1. All these components were mechanically stirred and then degassed under vacuum for 0.5 h until a uniform solution was formed. The solution was subsequently coated on the glass substrate and further cured at 80℃ for 4 h. The resulting coatings were transparent and had the thickness of 200 μm.

To observe the bidirectional migration phenomenon in real-time, images of the migrating process was captured by an optical microscope. A semiconductor cooler was attached on one side of the coating surface so as to control its temperature. Super-cooled circulating water was applied to help the heat elimination of the semiconductor cooler. The images of this process were captured by a charge-coupled device simultaneously.

Differential scanning calorimeter (PYRIS™ Diamond DSC, Perkin Elmer) was used to investigate the crystallization (phase transition) behavior of the pure alkane and silicone/alkane samples. The sample (5 mg) was first put in equilibrium at 25℃, then it was cooled down to -20℃ at cooling rate of 1 ℃ /min; after keeping it isothermal for 1 min, the sample was heated up to 25℃ at the same rate.

The deicing properties of the silicone coatings were evaluated by measuring the ice adhesion and ice accumulation on the coating surfaces respectively. The ice adhesion test was conducted to determine the force required to pull out a rod-shaped silicone sample from ice. The rod-shaped silicone rubber sample was inserted to an aluminum mold filled with deionized water, then the mold was placed in a freezer of -20℃ for 24 h until the water was completely frozen. The tensile test was carried out using a universal tensile testing machine (SANS CMT4104) equipped with a cold chamber. The testing temperature was set to -15℃ and the crosshead speed was 10 mm/min. The apparent

adhesion strength (τ) was calculated by dividing the maximum shear force (F_{max}) measured by the surface area of the rod embedded in the ice:

$$\tau = \frac{F_{max}}{\pi\, d\, l}$$

where d (~14 mm) is the diameter of the silicone rod and l (~45 mm) is the length of the rod embedded in the ice. At least 10 specimens for each sample were repeated to get reliable data.

The ice accumulation test was conducted in a freezer with the temperature of -20℃. A certain amount of super-cooled water was sprayed uniformly onto the glass plate, which was coated with pure silicone or silicone/alkane coating. The tile angle of the glass plate was 30° with respect to a horizontal plane. This action was repeated 10 times at an interval of 20 min. The ice accumulation on the samples can be obtained by measuring the weight difference of the coated glass plates before and after experiments.

Results and Discussion

The details of bidirectional migration behaviors of the silicone/alkane samples are measured quantitatively by a Differential scanning calorimeter (DSC) and illustrated in Fig. 1. As shown in Fig. 1a, for the *n*-tetradecane, there is a sharp exothermic peak in the cooling process, which is related to the alkane molecule crystallization. The freezing point of the *n*-tetradecane is measured to be 2.53℃ in this study. As the inverse process, an endothermic peak is observed in the heating process. The melting point of the *n*-tetradecane is 6.96℃, which is slightly higher than the freezing point measured above. In addition, the endothermic curve is observed to be relatively wider than the exothermic one. The difference between the exothermic and endothermic curves is usually explained as the ramp rate used in the DSC test. During the cooling process some imperfect crystal could be formed, which would be melted at lower temperature than the perfect one, and accordingly the endothermic peak becomes wider.

The DSC spectra of the silicone sample with/without alkanes are shown in Fig. 1b and 1c. Due to its amorphous structure, the pure silicone sample does not show any phase transition peak in the testing temperature range. However, the silicone samples doped with *n*-tetradecane present two exothermic peaks (Fig. 1c), which are quite different with the crystallization behaviors of pure *n*-tetradecane (Fig. 1a). The small and large exothermic peaks appear at -5.77℃ and -8.39℃, respectively. Note that due to the different thermal hysteresis of the samples studied, the silicone/*n*-tetradecane sample has lower freezing point than the pure *n*-tetradecane (2.53℃).

Ice adhesion force between a coating and ice is a key parameter in characterizing deicing ability of the coating. High adhesion force will increase the difficulty of removing accumulated ice and lead to aggravate ice accidents. As described in experimental section, the ice adhesion strength can be evaluated by using the pull-out method. The apparent adhesion strength of the tested samples is summarized in Fig. 2. The apparent adhesion strength of the pure silicone/ice is ~25 kPa. After addition of 20 wt.% alkanes, the values are decreased to ~16 kPa (for silicone/tetradecane) and ~13 kPa (for silicone/hexadecane), respectively. It is obvious that addition of the alkane molecules to the silicone matrix is a very effective way to reduce the adhesion force between ice and silicone rubber. It is illustrated in Fig. 2b that the alkane molecules diffused out of the silicone rod and formed thin layer around it at the testing temperature. Since the thin layer is very weak, it can be easily broken under tensile load, as indicated by the arrow in Fig. 2b. Following the breakage of the alkane layer, the adhesion between silicone rod and ice is completely destroyed. This would be the main reason why the alkane-modified silicone rod has the much lower apparent adhesion strength with ice in comparison with the pure silicone sample.

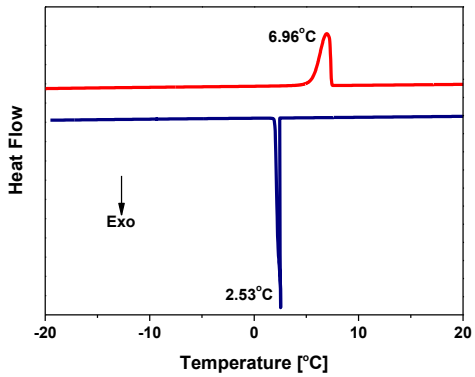
The deicing ability of the coating samples was further evaluated by the ice accumulation weight. It was conducted by spraying super-cooled water onto the tilted coating surface as described before. Pictures

shown in Fig. 3 were taken during the experiments to demonstrate the deicing ability of the samples. Several drops of ink were added to the super-cooled water for better observation. It can be found from Fig. 6a that the pure silicone coating is transparent at low temperature (-20 ℃) (left plate), whereas the silicone/alkane coating (right plate) becomes white due to the migration of the alkane molecules to the coating surface. It is also observed from the experiment that the water droplets slide easier from the silicone/alkane coating surface than from that of the pure silicone, which is possibly attributed to the fact that the former coating is rougher than the latter one, which may favor the movement of the water droplets. Fig. 3 illustrates the different morphologies of ice frozen on the two coatings. The ice accumulation weight ratio between the pure silicone coating and silicone/alkane coating is measured to be 5:1. More importantly, the coating samples exhibit different response to the external force such as a slight vibration. After slightly shaking by hand, the ice accumulated on the pure silicone coating almostly keeps invariable, while it easily falls off from the silicone/alkane coating, with some fragments of the alkane layer. This is also attributed to the very low adhesion force between alkane layer and silicone matrix. During vibration, the alkane layer is broken, which leads to the drop of the accumulated ice. After this process, there is no accumulated ice left on the silicone/alkane coating. This capability should be very useful in practice, since the wind blowing and even the weight of ice will cause the accumulated ice to fall off from the coating surface.

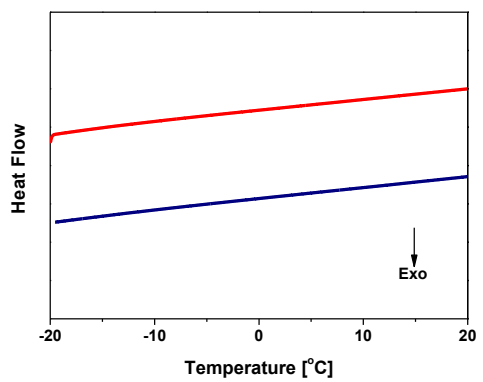
Conclusions

A novel deicing coating was successfully fabricated by introducing alkane molecule to silicone matrix via simple mechanical mix method. A so-called bidirectional migration effect of alkanes was observed, which means that the alkane molecules can come in or diffuse out of the silicone matrix under the influence of the environmental temperature. At lower temperature the alkane molecules migrated to the silicone coating surface, formed a hydrophobic and fragile thin layer, which had very low adhesion force with both the accumulated ice and the silicone matrix. Experimental results indicated that the apparent adhesion strength of the doped silicone dropped by 36-48%, as compared to that of pure silicone; and the accumulated ice almost completely fell off from the alkane doped silicone coating when subjected to slight vibration. Besides the silicone, the alkanes could be also added to other rubber systems to improve their deicing ability. This novel coating seems to have great potential in deicing engineering. So far, the major challenge is how to allow the alkane molecule to slowly release from the silicone matrix and prolong the coating's service life. For this purpose (to slow down the migration rate), a feasible way is to incorporate a certain amount of rigid particles to the silicone matrix. The related investigation is still ongoing.

Figure 1: DSC thermograms of (a) *n*-tetradecane molecule, (b) pure silicone and (c) silicone/*n*-tetradecane samples. The alkane content is 20 wt.% in the silicone/alkane sample. The blue lines represent the cooling curves, while the red ones represent the heating curves.



(a)



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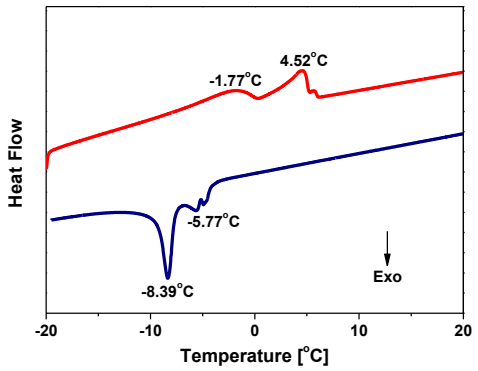
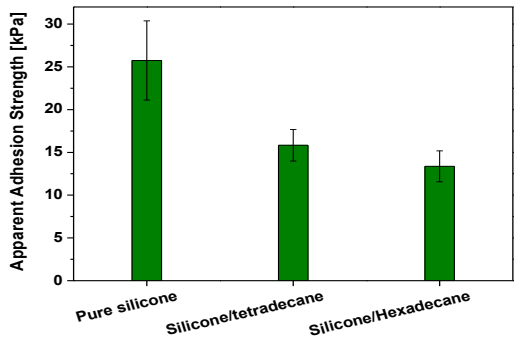
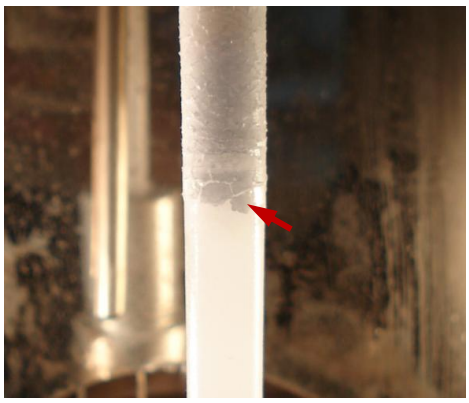


(c)

Figure 2: The tensile test results of the silicone/ice samples, which were obtained at tensile speed of 10 mm/min at -15℃. The alkane content is 20 wt.%. (a) the apparent adhesion strength between silicone rubber rod and ice; (b) an optical image of the silicone/alkane rod showing the alkane layer diffusing out of the silicone rod was broken under tensile load, as indicated by the red arrow.

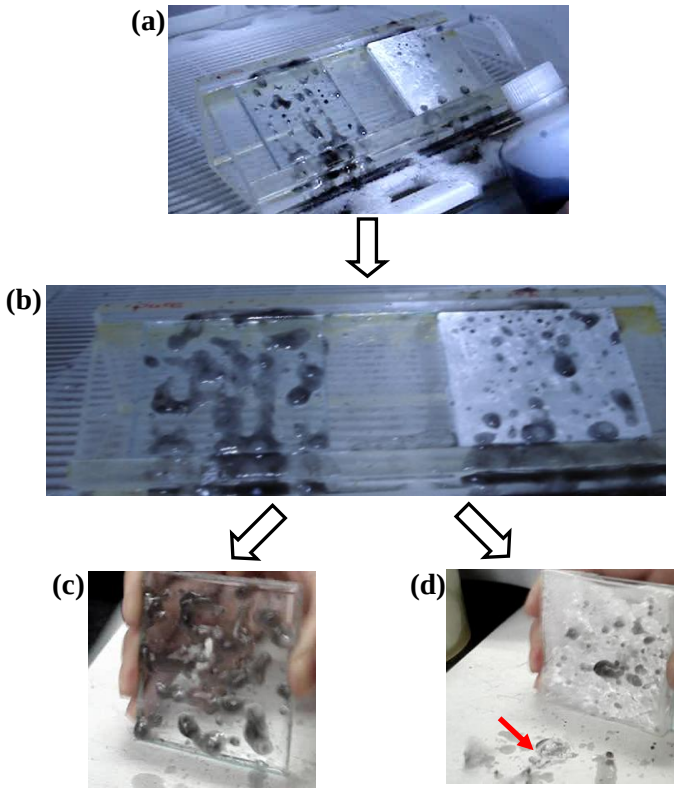


(a)



(b)

Figure 3: Optical images of ice accumulation demonstrating the deicing ability of the samples. The pure silicone coating (left plate) and the silicone/tetradecane (20 wt.%) coating (right plate) were coated on glass plates. The tests were conducted at -20 ℃ in a freezer. (a) Certain amount of super-cooled water was sprayed onto the pure silicone coating (left plate) and silicone/tetradecane coating (right plate); (b) accumulated ice on the pure silicone coating (left plate) and silicone/tetradecane coating (right plate); (c) After slight vibration the accumulated ice remains on the pure silicone coating (left plate) but falls off from the silicone/tetradecane coating (right plate); the red arrow indicates the broken ice with some fragments of alkane layer.



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