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Preparation and Characterization of a Thermal Barrier Heat-Resistant Silicone Coating

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ABSTRACT

In this study, a heat resistant coating with thermal barrier property was designed. Two types of silicone resin (based on methoxy methyl polysiloxane and methyl phenyl silicone resin) were used as thermal resistant binders, and the black iron oxide pigment and glass micro hollow sphere (MHS) additive were utilized to formulate the heat resistant/thermal barrier coatings. Coatings were applied to the steel substrates, and general properties of the coatings such as film formation, curing, and adhesion were then studied. The thermal stability of the coatings was evaluated by thermogravimetric analysis up to 450 °C. The thermal conductivity coefficient of the coatings was measured by temperature modulated differential scanning colorimeter (TMDSC). Investigation of the properties of all coatings showed that the silicone coating with the 7% of hollow microsphere had higher thermal stability ($T_{maximum\ weight\ loss}$= 538 °C) and better barrier properties (Thermal conductivity= 0.29 W/mK) compared with other coatings. Prog. Color Colorants Coat. 15 (2022), 65-73© Institute for Color Science and Technology.

1. Introduction

The thermal insulators can be considered as a solution to reduce energy consumption. Now a day, coating insulators have gained more scientific and technological attention. One of the upsides of these coatings is their resistance at high temperatures in addition to general properties. Many industries, e.g., oil, gas, petrochemical, have frequently used the insulative coatings in various applications. Hence, it seems essential to enhance and optimize the properties of the current organic/inorganic coatings. Silicone coatings showed the most optimal properties applied to high-temperature surfaces. Negligible water absorption, excellent durability, antibacterial properties, environmental sustainability, and abrasion resistance are the essential characteristics of these coatings [1, 2]. Silicone resins form durable, resistant, and hydrophobic networks that able to bond with inorganic surfaces. Silicone resins behave as an intermediate between the inorganic and organic material [3, 4].

Si-C and Si-O are the strong bonds that need high energy to break due to chemical processes such as degradation and decomposition. Besides, Si-C and Si-O bonds do not usually exist in nature, so their degradation in biochemical and biophysical processes is not likely. Silicone coatings are also highly resistant to chemical

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solvents and all types of fuels, Additionally, these coatings have excellent chemical resistance and high physical resistance [5, 6].

The hydrophobicity and resistance of these coatings to oxygen and ozone has made them one of the best candidate for weather-resistant coatings. The thermal degradation of silicone coatings forms a SiO_2 layer that is a stable and electrically insulator. Also, the high bonding energy in silicon resin chains makes the ultraviolet (UV) rays and heat, unable to degrade these kinds of coatings. Another reason for the high atmospheric stability of these coatings is the hydrophobic nature of the silicone resins, which limit the surface wettability by aqueous media [7].

One of the thermal resistant additives that have been utilized in these coatings is a hollow glass microsphere, which affects the thermal stability of the coatings by reducing the thermal conductivity. The impact of the micro hollow sphere (MHS) on the thermal conductivity of coatings is known, hence investigating the effect of this material on the thermal stability of the coatings may be helpful. Using a glass microsphere with particle sizes in the range of 10-100 microns as an additive in coatings offers many advantages. These particles generate a coating with a specific brightness and a beautiful appearance. They also control the viscosity of the coating and are the heat and sound insulation. Using these particles as a filler in the coating reduces the value of volatile organic compounds (VOC) because they do not absorb the resin, unlike other fillers. Based on the mentioned reasons, the use of microsphere in the surface coating industry is attractive. In the hollow microsphere, there is a vacuum inside most of the spherical particles that act as an insulation material. However, if the inside of the particle is filled with gas, the heat transfer at these particles will not occur through convection because the convection rate at porous materials can be neglected when the sphere diameter is less than 4 mm. The heat radiation is further emitted in vacancies by electromagnetic waves. Therefore, the heat transfer in insulative coatings containing microsphere can only be considered by thermal conductivity [8, 9].

In this research, the thermally stable coating has been formulated with thermal barrier properties. Some other researchers [10, 11] have performed an analysis of the thermal stability of coatings containing silica nanoparticles. They observed that the thermal degradation and maximum decomposition temperatures of the coating were observed with the increase in silica nanoparticle content. Coatings also showed higher residue due to the presence of the nanosilica particles.

Accordingly, in this research work, the effect of the glass microsphere on the coating properties has been investigated. The properties of the prepared thermal barrier coatings containing microsphere were further compared with the coating properties without this additive.

2. Experimental

The initial properties of film formation, heat resistance, curing, and adhesion behavior of two types of silicone resins were investigated in the pre-experimental tests. Specimens with appropriate characteristics were then selected, and other tests, e.g., adhesion, thermal conductivity, and physical properties of the specimens, were also conducted.

2.1. Materials

In this study, two types of silicone resins (REN 60 and silicon MSE 100), were obtained from Wacker Company, USA. Some detailed specifications of these resins are presented in Table 1. The Micro hollow sphere (MHS) employed in this study was manufactured by 3M, USA, which has the following characteristics in Table 2. Thermal stable pigment such as Black iron oxide (Fe_3O_4) was supplied by Huntsman Company, USA, with 1300 °C thermal stability. Talc (chemical formula ($Mg_3(OH)_2/Si_4O_{10}$)) was prepared by Sibelco Company, UK, with 1000 °C thermal stability as a filler. Copolymer of methyl hydroxyloxane-dimethyl siloxane was used as a catalyst to accelerate the networking of silicon resin at ambient temperature.

2.2. Preparation of coating

Two types of coating were prepared using two different kinds of resin and a thermally stable pigment. Moreover, three types of coating were prepared using different weight percentages of MHS (2, 4, and 7% by weight). Thermal stability and adhesion tests were performed on coating films. Tables 3 and 4 illustrate the formulations of coatings with thermally stable pigments and a micro hollow sphere.

Table 1: Specifications of the silicone resins.

Code	Chemical structure	Baking condition	Heat resistance (°C)	Appearance
Si-60	Methyl phenyl group-containing silicone resin solution in xylene	Surface drying at ambient temperature in the presence of a catalyst or 200 °C	Up to 400 °C in the presence of heat resistant pigment	Low viscosity, flexible and hydrophobic film, bright yellow
Si-100	Methyl ester of a mixture of different oligomeric methyl silicates	Curing at ambient temperature in the presence of moisture or catalyst	Up to 400 °C in the presence of heat resistant pigment	Low viscosity, solvent-free, colorless

Table 2: Characteristics of a micro hollow sphere.

color	Size (µm)	pH	Thermal conductivity (W/mK)	Density (gr/cm^3)	Oil% absorption	Hardness Mohs
white	50-60	7-8	0.03	0.3-0.6	10-20	3.5-4

Table 3: The formulations of coatings containing thermally stable pigments.

Sample code	Type of resin	Resin (w%)	Benton Gel (w%)	Black iron oxide (w%)	Talc (w%)	Xylene (w%)
BL Si-60	Si- 60	50	5.5	7	5	32.5
BL Si-100	Si- 100	50	5.5	7	5	32.5

Table 4: The formulations of coatings containing MHS.

Sample code	Type of resin	Resin (w%)	Benton Gel (w%)	micro hollow sphere (w%)	Xylene (w%)
HS 2	Si- 60	88.2	5	2	5
HS 4	Si- 60	86.4	5	4	5
HS 7	Si- 60	83.7	5	7	5

The pigments were primarily dispersed in the resin (by Pearl mill) to make the coating. Proper amounts of the wetting and dispersing (anti terra, BYK) additives were used to disperse the pigments. The pigment paste was mixed with other components when the particle size reached below 20 microns.

However, there are two problems reported by researchers [8, 9] regarding the preparation of the coatings containing microsphere. The first problem is related to the sensitivity of the microsphere to shear stresses. They may break during dispersion. In this study, a mixer with a speed of 1200 rpm and at a dispersion time of 30 minutes was considered for breaking the HGMs.

Furthermore, the temperature and viscosity may have an insufficient effect on breaking of more than 80% of the microsphere. The second problem is associated with phase separation and the possibility of particle settling, which is commonly observed in high build coatings. The distribution of the microspheres is directly related to their thermal barrier effect in the coating. Therefore, a light microscope was utilized to investigate the particle size distribution of the coating following the microsphere dispersion.

Resin dispersion and catalyst were mixed at a ratio of 1: 100 in order to prepare coating films. The steel substrates were cleaned and degreased with acetone before the coating application. The samples were then dried for 30 min at 70 °C. Samples were baked for one more hour at 80 °C. The dry film thickness of the coatings was 170 ± 10 microns.

2.3. Test methods

All coatings were first evaluated in terms of appearance, curing and film formation, adhesion behavior, thermal resistance, and physical properties. Afterward, four samples with initial conditions were compared in terms of heat conduction. The following elucidates the test methods. Some tests were repeated according to the standard at regular times.

2.3.1. Adhesion

The cross-cut test was used to evaluate the adhesion of the coatings on the substrate according to the standard (3359 ASTM D).

2.3.2. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) was carried out using a Pyris Diamond SII model, made by the Perkin Elmer Company, USA. The weight loss of coating was determined due to heating the sample. The test was carried out under a nitrogen atmosphere at temperatures of 25 ℃ to 1000 °C and a heating rate of 10 °C/ min.

2.3.3. Thermal stability

The coating samples were heated in the furnace (Ceram Sanat Co. Iran) at a rate of 10 °C /min to 650 °C. Finally, the appearance and adhesion of the specimens were evaluated at room temperature.

2.3.4. Differential scanning calorimetry

The thermal conductivity of the samples was evaluated using differential scanning calorimeter, Polyma 214, Netzsch Co., Germany. This method is based on determining the heat transfer rate of a sample [12-14]. Therefore, the sample was placed into the sample holder furnace of the calorimeter; moreover, a calibration substance such as indium was placed on top of the sample. The reference furnace was kept empty (Figure 1).

During the melting of the calibration substance, the temperature of the calibration substance must be constant. A scan was performed to measure the differential power produced during the melting of the calibration substance. The obtained curve had an approximately linear increase during the melting and an exponential reduction after melting (Figure 2). The slope of the curve allowed us to calculate the sample's thermal conductivity. Solving the heat differential equation is ruled by the following equation 1 [12-14]:

$$\text{Slope} = \frac{d\Delta P}{dT_P} = \frac{2}{R} \quad (1)$$

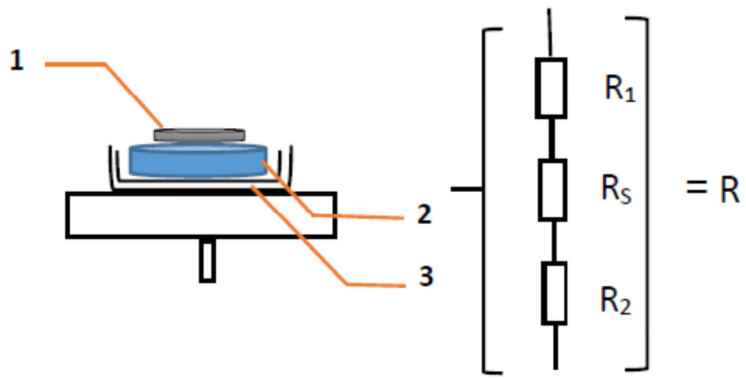

Figure 1: Sample geometry and its block diagram; 1: indium; 2: cylindrical sample; 3: DSC cell; R, total thermal resistance; R_1, R_2, thermal contact resistance.

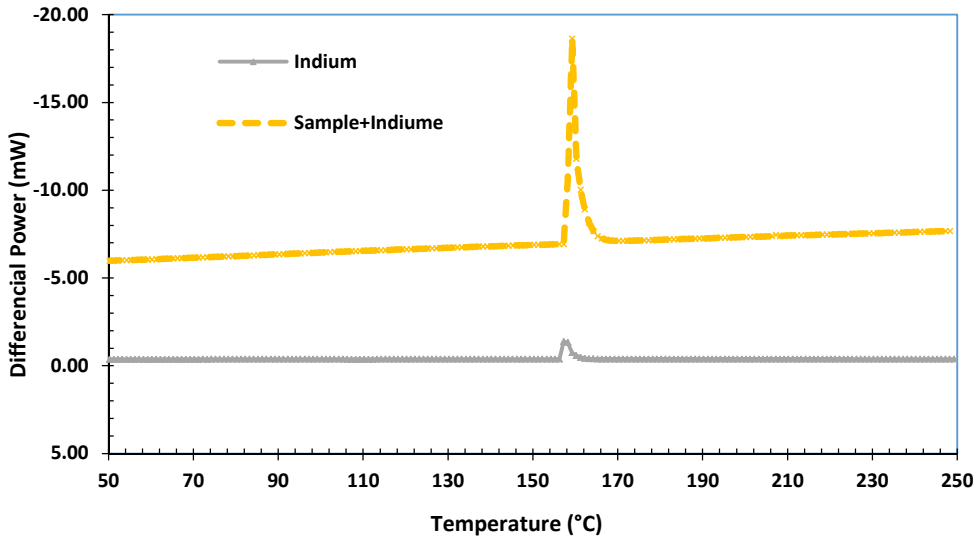

Figure 2: The curve obtained for a scan of the sample having an indium disk on its top.

where P is the differential power of the calorimeter obtained from the subtraction of the zero lines, T_P is the predefined temperature of the calorimeter, and R is the overall thermal resistance (Eq. 2) [12, 14]:

$$R = R_1 + R_2 + R_S \quad (2)$$

where R_1 is the thermal contact resistance between the sample and the sample furnace, R_2 is the thermal contact resistance between the sample and the calibration substance, and R_S is the thermal resistance of the sample (Eq. 3) [12, 14]:

$$R_S = \frac{L_S}{\lambda_S A_S} \quad (3)$$

where L_S, λ_S, A_S are the height of the sample, its thermal conductivity, and the area of a horizontal cross-section of the sample, respectively. Eq. (1) indicates the smaller thermal conductivity, the lower slope of samples.

To measure the thermal conductivity of a material, it is necessary to repeat the experiment with samples of different known heights and constant cross-sectional areas. Assuming the samples have the same thermal contact resistance $R_1 + R_2$, according to Eqs. (2) and (3), the total thermal resistance is a linear function of the L_S/A_S ratio. Thus, a plot of the overall thermal resistance versus the L_S/A_S ratio is a straight line. The inverse of the slope is equal to the λ_S thermal conductivity of the material, and the ordinate intercept is similar to the sum of $R_1 + R_2$ [12-14].

To evaluate the thermal conductivity, we applied coatings with different thickness films. These films had to cover the pan surface of the apparatus thoroughly. Afterward, a certain amount of reference substance (Indium, 11.24±0.1 mg, scan rate: 10.0 ± 0.3 K.min^{-1}) was applied on the coating surface. Measurements were repeated twice for each coating and finally averaged. The thermal resistance of the sample (170 micrometer free films) was determined from equation 1.

3. Results and Discussion

3.1. Investigation of the dispersion of MHS particles in the resin matrix

It is well known that the properties of the micro hollow spheres in the resin matrix are strongly dependent on the distribution of MHS in resin [15]. The optical microscopic technique shows well dispersion of MHS particles in the matrix, and no accumulation was observed (Figure 3).

3.2. Adhesion

A cross-cut adhesion test was performed at room temperature and 450 °C. The results are shown in Table 5. According to Table 5, all samples except Bl Si 100, the adhesion and thermal stability up to 450 °C properties were almost identical and acceptable. Therefore, this sample was not considered for the next experiments. As mentioned before, above 250 °C temperatures, organic groups of silicon resin are decomposed. When all the organic components are decomposed during heating, the residual is an inorganic compound ($(SiO_2)_n$ structure). This layer has a high adhesion strength to the substrate [16, 17].

Table 5: Cross-cut adhesion of the samples.

Sample code	Specifications	Primary adhesion	Adhesion after heating to 450 ℃
Si- 60	Silicone clear coat	5b	5b
Bl Si-60	Silicone black coating	5b	5b
BL Si-100	Silicone black coating	5b	3b
HS 2,4and 7	Silicone coating containing microsphere	5b	5b

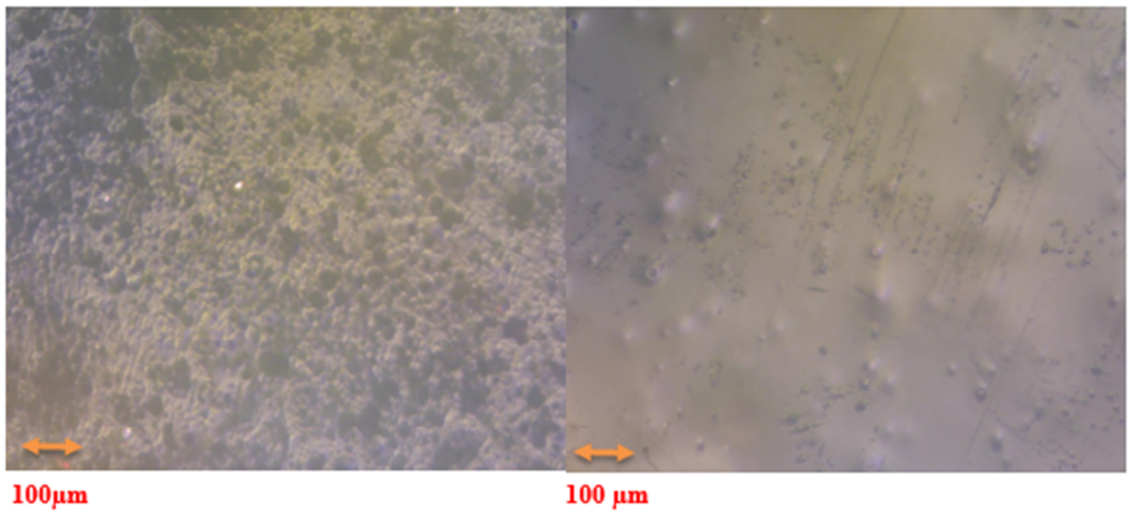

Figure 3: Optical microscopic images of specimens containing microspheres samples containing 7 % microsphere (left) and 2 % microsphere (right).

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed to investigate the thermal resistance and examine the weight loss of the samples due to the rising temperature. Weight loss in organic coatings can reflect the physical and chemical processes in the network structure caused by temperature rise. The results of the thermogravimetric analysis of different samples are shown in Figure 4. The test data should be normalized based on the weight percentage of pigment and MHS in the coatings.

As shown in Figure 3, all samples have 5 % weight loss at approximately 250 °C, possibly indicating the evaporation of residual solvents in the coating film. From 300 to 400 °C, 10% weight loss is observed in the coating. This amount of weight loss can be attributed to the thermal decomposition of the organic part of the resin, which is removed from the coating film at this temperature range while the inorganic part of the resin remained unchanged [16]. As Figure 3 shows there is no degradation before 450 °C. The temperature corresponding to 10 wt% weight loss was used as a thermal stability index ($T_{10\%}$), and the char yield at 800 °C was employed as an index for the final thermal stability properties (Y_c). The temperature at which the maximum sample weight loss occurred (T_{max}) was extracted from the derivative diagrams of weight loss. All related data are listed in Table 6.

Table 6: Data of TG and DTG.

Sample code	$T_{10\,\%}$ (°C)	T_{max} (°C)	Y_c at 800 °C (%)
Si 60	404	508	32.2
Bl Si60	406	517	34.9
HS 2	410	519	35.2
HS 4	413	527	42.5
HS 7	400	538	44.9

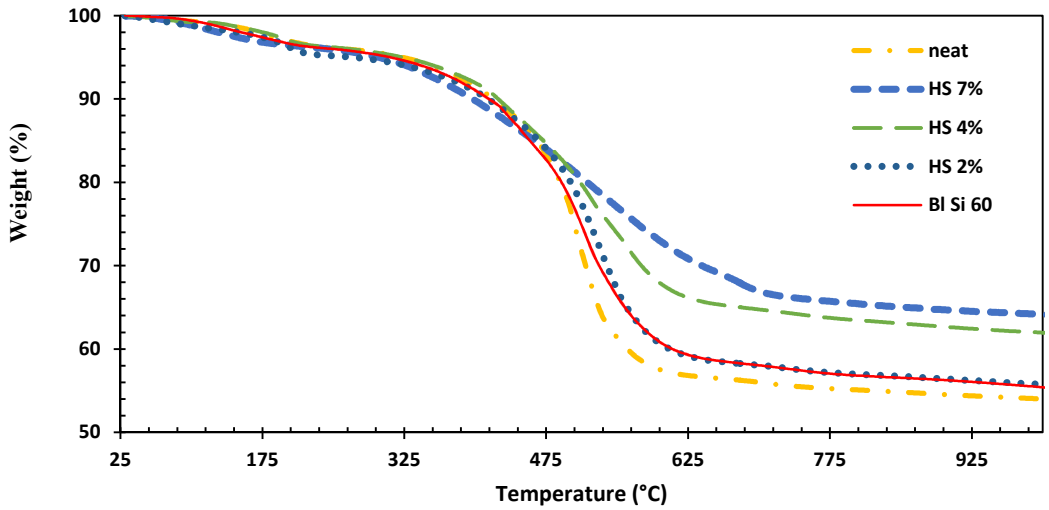

Figure 4: Weight as a function of increasing temperature for different samples.

According to Table 6, 10 wt% weight loss occurred in all samples at 400-413 °C. Based on the same table, the lowest weight loss in the resin matrix belonged to the samples containing 7 and 4 % wt. of the microsphere, and the highest weight loss was further observed in the silicone resin sample. This indicates that the increase in the amount of microsphere in coatings can result in increased thermal stability. Table 6 also shows that the presence of thermally stable pigment had less effect on the thermal stability compared with MHS at 800 °C. Moreover, the best thermal stability was observed in samples containing 7 and 4 wt % of the microsphere and the lowest thermal stability was observed in the neat sample. This trend was actual for samples at 400 °C. With the increase in the content of MHS, the temperature of maximum weight loss increased from 519 to 538 °C, probably owing to the ether interaction between the spheres and resin matrix [15, 19]. Furthermore, the char yield at 800 °C augmented with the increase in the MHS content, indicating a marginal increase in the thermal stability of coatings because the lowest char yields of all samples at 800 °C is a neat sample (silicone resin).

3.4. Differential scanning calorimetry (DSC)

The differential scanning calorimeter was used to determine the thermal conductivity of the samples according to the available methods; the results are presented in Table 7 [19, 13, 20]. Based on Table 7 and comparing its data with the thermal stability of samples, it can be stated that increased thermal barrier additives (MHS) in the formulation of coating reduced the thermal conductivity.

Table 7: Thermal conductivity of samples.

Sample	Thermal conductivity(W/mK)
Si 60	0.37
Bl Si60	0.4
HS 2	0.25
HS 4	0.28
HS 7	0.29

4. Conclusion

A series of formulation with silicone resin and thermally stable and thermal barrier pigments and additives were employed to investigate the thermal properties of the coatings. It was found that the silicone resins could be used as a binder for thermally stable coatings owing to their high Si-bond energy and excellent physical-mechanical properties. The presence of heat-resistant pigment in the resin structure increased the thermal resistance of the coating Therefore, a hollow microsphere could improve thermal stability and the thermal barrier properties of the coatings. The results of the tests showed that the organic groups in the silicone resin network started to decompose at temperatures above 250 °C, and at the end, an inorganic lattice with a $(SiO_2)_n$ structure remained on the substrate, forming a chemical bond with the substrate and result in increasing its hardness and adhesion.

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