Interfacial bonding enhancement of the RTV recoating with sandwiched contaminant by plasma jet

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Abstract: Room temperature vulcanised (RTV) silicone rubber is widely used in electrical power system, applied to the glass or porcelain insulator surface to enhance insulation. RTV coatings get contaminated after long-term operation and need to be recoated. Contaminants accumulate and embed into the surface of base RTV coating, forming a hard-to-remove inorganic transition layer. Such sandwiched contaminant layer destroys the adhesion between original and reapplied silicone rubber coating greatly. Authors’ study innovatively reports a method to enhance interfacial bond properties of the RTV recoating with sandwiched contaminant layer, by using an atmospheric-pulsed discharge plasma jet (APPJ) for surface treatment. Water boiling test and 180-degree peel test were conducted to evaluate interfacial bond properties macroscopically. Scanning electron microscopy (SEM) was applied to observe the cross-section of recoating interface, while Fourier-transform infrared spectroscopy (FTIR) to detect chemical changes of contaminant layer, giving out microscopic and theoretical explanation.

1 Introduction

Room temperature vulcanised (RTV) silicone rubber is widely used to avoid serious pollution flashover accidents [1–3]. After long-term outdoor service in some heavy-polluted areas, RTV coating lost hydrophobicity and hydrophobicity transfer, resulting in decrease of anti-fouling performance, thus needing to be recoated. However, pollutants accumulate over a long period on the surface of RTV coating and embed in it [4–6]. The contaminant forms a transition layer with original RTV coating and is hard to remove. If recoating is carried out when the natural contaminant is not treated, the original/transition/reapplied RTV layer forms a complex, sandwich-like structure. Presence of the sandwiched contaminant layer has adverse effect on the bonding of the two RTV layers. The contaminant seriously destroys the adhesion between original coating and reapplied RTV coating, and bonding interface gets pore structure [7], reducing the reliability of electric distribution systems.

In order to achieve the ideal bonding of RTV recoating with sandwiched contaminant, specialised cleaning is needed to remove the surface contaminants and also interpenetrating polymer networks or molecular bridge technologies may be carried out to perform the restoration treatment of base coating. Plasma surface modification, as one of the most common surface treatment methods, has been widely used to promote adhesion process through cleaning, etching, and functionalisation of a wide range of surfaces [8–13]. Atmospheric low-temperature treatment was found to significantly improve the adhesion between neoprene rubber and aluminium plate [14]. Mauro [15] found that atmospheric pressure plasma (APP) treatment was efficient in grafting oxygen atoms to the carbon surface, helping the adhesion process of surfaces for composite production. Plasma treatment has great influences on surface properties of silicone rubber [16, 17]. Wang [16] found that short time (<3 min) of plasma treatments mainly remove pre-existing low molecular weight (LMWs) siloxanes on PDMS surface and the silica-like layer is formed after 3 min or longer time of treatments. Plasma was used for surface clean and surface activation in these previous studies. Plasma clean processing involves change of chemical composition and structure of the surface, while for surface decontamination, plasma removes organic pollutants physically and oxidise them to removable matter such as carbon dioxide.

However, the surface condition of the contaminated RTV layer differs greatly from these above-reported researches. RTV silicone rubber has a low surface energy and is hard to adhesion. Sandwiched contaminant is embedded and forms a transition layer with original RTV coating. Contaminant layer contains non-soluble components, such as inorganics and soluble salts, exhibits a multi-aperture and irregular surface structure with agglomeration and micro-convexities, where tiny dust and static charges might be trapped and accumulated. Contaminated surface cannot be well penetrated by reapplied RTV coating, resulting in few intermolecular contact and weak interfacial bonding. The reapplied RTV coatings contains solvent, which is supposed to be absorbed on the substrate’s surface, resulting in slight swelling and dissolution, thus forming an interpenetrating polymer networks at the interface. However, the existence of sandwiched contaminant layer is hard to be penetrated, thus obstructing interfacial bonding. Research on interfacial bonding enhancement of the RTV recoating with sandwiched contaminant has seen little report.

In the light of above, this paper innovatively reports a method to significantly enhance interfacial bond properties between the RTV coating with sandwiched contaminant and reapplied LSR coating, by using an atmospheric-pulsed discharge plasma jet (APPJ) for surface treatment.

2 Experimental setup

An APPJ was proposed to treat contaminated RTV coating. Fig. 1 shows the schematic of the APPJ device used in this paper.

Argon gas was supplied through a quartz tube, and the gas flow rate is regulated with a mass flow controller. A quartz glass tube with inner diameter of 8 mm and outer diameter of 10 mm was used as a dielectric barrier. High-voltage electrode was a diameter copper rod confined coaxially in the centre of the tube. A metal foil in contact with the outside surface of the tube served as the ground electrode.

3 Experimental results

3.1 120 °c boiling water test

RTV rubber sample was prepared by first extending 50 g liquid RTV evenly on a clean glass substrate. One hour later, artificial contaminant was spread evenly through a sieve onto RTV coating.
Contaminated samples’ surface got a large blistering area (b1), indicating moisture destroying the adhesion of the two layers. However, as plasma treatment time gradually increased to 50 s, the blistering area quickly decreased and the bubble size was reduced to be smaller (b2–b6). These results proved that plasma exposure significantly strengthened the adhesion of RTV recoating with sandwiched contaminant for a suitable treating time.

### 3.2 180-degree peel test

The 180-degree peel test, according to the standard [19], is used to determine the peel resistance of a bonded assembly between one rigid adherend and one flexible adherend.

Fig. 3(A) is a typical schematic of finished sample. Quantitatively applied RTV on a glass strip. One hour later, spread contaminant on the coating as described in Section 3.1.1. NSDD of the pollution was set 1.0 mg/cm\(^2\) and SDD was set 0.1 mg/cm\(^2\). After 72 h, treat samples with plasma. Covered the sample with a long strip of clean industrial non-woven mesh cloth, which provided drawing position in the following peel test. Then, perform recoating. After reapplied coating solidified completely, conducted peeling test. Each experiment was carried out for three times. Fig. 3(B) shows a typical curve of the peel force versus displacement.

Table 1 shows the results of 180-degree peel test at varying supplied voltage and frequency. As can be seen, average peel strength ($\sigma_{180}$) of recoated clean samples was 5.30 N·cm\(^{-1}\), decreased by the accumulation of sandwiched contaminant to 2.87 N·cm\(^{-1}\). $\sigma_{180}$ increased if the original layer was pre-treated with plasma jet before recoating. For example, when the applied frequency increased from 25 to 40 kHz ($U = 10$ kV), $\sigma_{180}$ increases from 3.86 to 4.54 N·cm\(^{-1}\), and a 58% increase is obtained. In addition, $\sigma_{180}$ increases from 3.54 to 4.24 N·cm\(^{-1}\) when applied voltage increased from 6 to 12 kV. These results proved that the plasma treatment significantly enhance the interfacial bonding of RTV recoating.

### 3.3 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) was used to study the bonding interface morphology before and after plasma treatment. Fig. 4(f1–f5) shows the cross-section morphologies of coating/substrate interfaces, with magnification factor at 500 while f6 at 5000. Recoating interface of clean sample showed unclear boundary ($\sigma$1), indicating ideal bonding performance obtained. Before plasma treatment, recoating interface with sandwiched contaminant showed apparent boundary, where particles and cracks could be seen clearly ($\sigma$2), indicating sandwiched contaminant layer was hard to be penetrated by reapplied RTV coating. After plasma treatment, cracks were filled adequately and recoating interface showed unclear boundary, which indicates sandwiched contaminant layer was well penetrated by reapplied RTV coating and the bonding was tight ($\sigma$3–f6).

### 3.4 Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was then used to assess chemical changes of coating surface and a typical spectrum was shown in Fig. 5.

Compared with the untreated sample, peaks of plasma treated sample at 2960, 3300, and 3600 cm\(^{-1}\) were significantly increased, correlated to hydroxyl and methyl groups, respectively. The increase of the broad absorption peak centred at 3300 cm\(^{-1}\) and the peak between 1600 and 1700 cm\(^{-1}\) after exposure to plasma jet indicated the formation of hydroxyl and carbonyl groups, respectively. In addition, an increase in the plasma power frequency increased these absorption bands.
4 Discussion

As is known that contaminant layer stained on RTV surface was porous, with an irregular surface structure, which leads to the accumulation and trapping of static charges, thus resulting in agglomeration and particles. The particles were attracted to one another via static charges on the particles’ surface, forming a high-energy surface. However, the reapplied RTV coating exhibited a lower-surface-energy surface. Good bonding requires equal surface energy between sandwiched old layer and recoating, to eliminate the imbalance of surface intermolecular forces. In addition, present of the sandwiched contaminant hindered migration of LMW siloxanes form silicone bulk to the contaminated surface (Fig. 6(A)). Thus, reapplied RTV coating can hardly penetrate into the contaminant layer, forming little interfacial bonding during cohesive bonding process, resulting in only few intermolecular point contacts, which lead to particles and gaps observed in Fig. 4(f2). This result is also in accordance to the larger blistering area (Fig. 2(b1)) and the 46.05% decrease in average peel strength (Table 1, c1).

Plasma exposure of the sandwiched contaminant layer has significant effect on the surface characteristics. During the treatment, active plasma species was blown onto contaminated coating surface, causing particle collision, and energy injection. It has been proved that atmospheric air or helium plasma jet could rapidly improve hydrophobicity of contaminated silicone rubber surface in several seconds, by accelerating the transfer of uncross-linked LMW siloxanes to the component of contamination layer surface and absorbed to it [20–23]. Out-migrant LWMs may offer substantial binding sites for liquid recoating, resulting in better bonding performance. Accordingly, adhesions between original and reapplied RTV coating are strengthened and the interface boundary becomes unclear in Fig. 4(f3–f6). These findings, combined with the data obtained by boiling water test (Fig. 2(b2–b6)) and 180-degree peel measurements (Table 1, d1–4, e1–4), strongly support the idea of possible chemical crosslinking reaction occurred during the recoating processes.

This suggested that Ar plasma jet treatment induced surface oxidation by insertion or substitution of polar groups like hydroxyl, carbonyl, or silanol (Fig. 6(C–E)). These oxygen content polar groups might offer reactants for cross-linking reaction by dehydration and condensation, as given by equation (a) and (b) (Fig. 6), resulting in the formation of interpenetrating polymer networks. Possible evidence has been presented in prior studies which indicates that the strength of the adhesive bond is promoted because via the reactions with polar groups formed [20–23]. Detailed mechanisms will be fully studied in the future studied.

5 Conclusions

In the present investigation, effects of the plasma treatment on the adhesion between contaminated coating and reapplied RTV coating are studied. Then, it is found that sandwiched contaminant hindered migration of LMW siloxanes form silicone bulk to the contaminated surface (Fig. 6(A)). Thus, reapplied RTV coating can hardly penetrate into the contaminant layer, forming little interfacial bonding during cohesive bonding process, resulting in only few intermolecular point contacts, which lead to particles and gaps observed in Fig. 4(f2). This result is also in accordance to the larger blistering area (Fig. 2(b1)) and the 46.05% decrease in average peel strength (Table 1, c1).

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Table 1

| No. | NSDD, mg cm⁻² | U, kV | F, kHz | Time, s | σ₁₈₀°, N cm⁻¹ | Increase |
|-----|---------------|------|--------|---------|---------------|----------|
| c0  | 0             | 0    | 0      | 0       | 5.32          | NA       |
| c1  | 1.0           | 0    | 0      | 0       | 2.87          | NA       |
| d1  | 1.0           | 6    | 30     | 100     | 3.54          | 23%      |
| d2  | 1.0           | 8    | 30     | 100     | 3.90          | 36%      |
| d3  | 1.0           | 10   | 30     | 100     | 4.08          | 42%      |
| d4  | 1.0           | 12   | 30     | 100     | 4.24          | 47%      |
| e1  | 1.0           | 10   | 25     | 100     | 3.86          | 34%      |
| e2  | 1.0           | 10   | 30     | 100     | 4.13          | 44%      |
| e3  | 1.0           | 10   | 35     | 100     | 4.32          | 51%      |
| e4  | 1.0           | 10   | 40     | 100     | 4.54          | 58%      |

Fig. 4 SEM results of RTV samples (size: 5 × 5 cm²) treated by plasma for 3 min supplied by 30 kHz frequency power. NSDD = 1.0 mg/cm², SDD = 0.2 mg/cm²

Fig. 5 Fourier transform infrared spectrometry of contaminant layer on base RTV coating, treated for 3 min supplied by 10 kV voltage power. NSDD = 1.0 mg/cm², SDD = 0.1 mg/cm²

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RTV recoating, especially in heavy-polluted areas, which is of great significance for improving the safety of power system. However, further investigation needs to be launched to clarify the interaction mechanism between plasma and sandwiched contaminant layer and interfacial bonding process of RTV recoating in more detail.

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7 References

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