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Selection of silane coupling agents for improved adhesion of polyurethane-based coatings filled with silicone rubber nanoparticles

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Increased usage of pure tin (Sn) or Sn-rich alloy in Pb-free electronics results in putting more risk for the spontaneous growth of tin-whiskers. These whiskers can be mitigated by applying a conformal coating over the metal surface. Of all the material properties, adhesion strength of the conformal coating over the tin surface is crucial in mitigating the growth of tin whiskers. But the adhesion between dissimilar materials such as conformal coating (organic) and tin (inorganic) is often challenging. Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. The main goal of this paper is to investigate the effect of silane coupling agents on the adhesion behavior of polyurethane (PU) and polyurethane acrylate (PUA) on the tin solder pads. Adhesion behavior of PU and PUA coatings filled with silicone rubber (SR), which makes these coatings more ductile and tougher, was also investigated. It was found that an isocyanate-based silane coupling agent provided excellent adhesion for PU and PU+SR based conformal coatings and an acrylic-based silane coupling agent for PUA and PUA+SR coatings on the tin surface. This was due to the reaction bond formation between the silane coupling agent and the coating. Hence, the selection of silane coupling agents with organofunctional group similar to the coating material is crucial to improve the adhesion properties of the coating.

Introduction

The European Directive on restrictions of hazardous substances legislation prevents the use of lead (Pb) in electronics.[1] This is driving the industry to use pure Sn and other high Sn content alloys with no Pb. However, the use of tin rich alloy results in the spontaneous growth of needle-like tin whiskers.[2] While the potential mechanisms for the formation of tin whiskers were identified, there seemed to be no universal solution to get rid of these whiskers. As a result, the formation of these whiskers has been mitigated by using several metallurgical techniques with limited success.[3] Conformal coating can, however, provide a more effective way to mitigate the tin whisker growth.[4] This is because the conformal coatings are used to protect the electronics assembly from corrosive and chemical materials and minimize the environmental stress on the circuit boards,[5] which can simultaneously contain or eliminate the tin whisker growth effectively due to its complete coverage over the tin surface.[6]

Amongst the commercially available conformal coatings, polyurethane (PU) offers excellent moisture and chemical resistance.[7] It has the segmented polymer structure consisting of hard (isocyanate) and soft (long chain polyol) parts that give it adjustable mechanical properties and make it a suitable candidate for coating applications.[8–10] Polyurethane acrylate (PUA) has also received attention in more recent days because of the UV-curable system that provides a rapid and environmental friendly curing process.[11] Extensive research has been conducted to enhance the mechanical properties of PU and PUA conformal coatings.[12,13] Despite the efforts, whisker growth has been observed in coating with poor adhesion strength.[12] This was due to the delamination of the coating from the tin surface, which resulted in a gap between the surface of the tin and the coating, thereby providing a space for the subsequent nucleation and growth of tin whiskers.[12,13] Considering the importance of the adhesion strength, limited research have been published on the improved adhesion of PU/PUA conformal coatings.[14]

Polyurethane nanocomposite materials have been adopted to increase the mechanical strength and thermal stability of the coating in recent applications.[4] The filler particles contribute to the strength of the matrix due to the composite strengthening effect of the harder particles in the matrix. On the other hand, silicone rubber has low hardness, low modulus, and high total elongation, which make it an excellent candidate to enhance the ductility of rigid PU/PUA coatings.[15] However, the addition of these filler particles has shown to decrease the adhesion strength of the coating on the metallic surface.

Silane coupling agents have the ability to form a strong bond between organic and inorganic materials.[16] Silane coupling agent has a general formula $[\mathrm{R{-}(CH_2)_n - Si - X_3}]$ showing the two classes of functionality. X (head of the silane agent) is a hydrolysable group typically alkoxy, acyloxy, halogen or amine. Following this is a reactive silanol group, which can condense with other silanol groups. A linker is used to connect the silicon atom and the organic group. The R (tail portion of the silane agent) group is an organic group that may possess a functionality that imparts desired characteristics for adhesion promotion.

In this research, several potential silane coupling agents were used at tin surface in an attempt to improve the adhesion of the PU and PUA conformal coatings to tin. The effect of these silane agents was further investigated for the same coatings dispersed with silicone rubber nanoparticles. These nanoparticles were adopted as an enhancer for mechanical properties of the PU and PUA coatings whose adhesion needed to be warrantied.

Experimental Procedure

Materials

Commercially available PU and PUA resins (PC18M and PC40UMF, respectively, from Henkel Inc, Irvine, CA) were used in this study. PC18M had 70% PU and 30% solvent and PC40UMF had less than 1% of solvent. Albidur PU 5640 (from Evonik Corporation, Parsippany, NJ) were the silicone rubber particles (100 – 300 nm in size) added to the PU/PUA resin. Albidur PU 5640 contains 40 wt-% silicone spherical particles dispersed in PPG-triol. The specially designed coupons were provided by Honeywell FM&T (National Security Campus, Kansas City, MO). The silane coupling agents (from Gelest, Inc., Morrisville, PA) used in this investigation are mentioned in table 1.

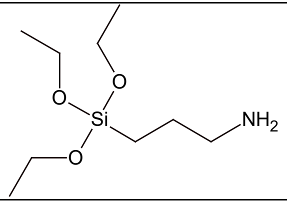
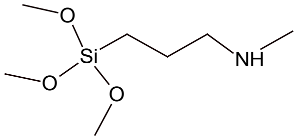
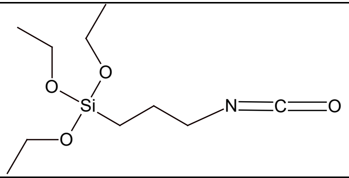
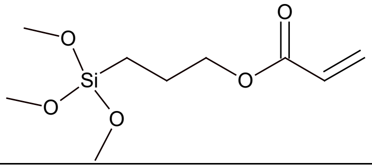
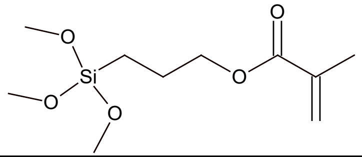
SILANE COUPLING AGENT TYPE	**SILANE COUPLING AGENT NAME**	**CHEMICAL STRUCTURE**
Amine based	Aminopropyltrimethoxysilane (APTES)	
	N-Methylaminopropyltrimethoxysilane (MAPTS)	
Isocyanate based	3-Isocyanatopropyltriethoxysilane (IPTES)	
Acrylate based	3-Acryloxypropyltrimethoxysilane (APS)	
Methacrylate based	Methacryloxypropyltrimethoxysilane (MPS)	

Table1: List of silane agents and its chemical structure used in this study.

Silane treatment

Coupons were treated with air plasma for 30 minutes for both cleaning and Sn surface activation by generating the –OH group on its surface. After plasma treatment, the coupon was soaked in the respective silane solution (2 wt.% of silane coupling agent in DI water) for 2 hrs, during which hydrolysis reaction was controlled by acetic acid (under pH ≈ 4). The coupon was then taken out and dried at 60 °C for 3 h.

Sample preparation

2.5 g of Albidur PU 5640 resin was added to 28.5 g of PC18M resin and stirred at room temperature for 5 minutes to get PU+5SR solution with PU:SR equal to 100:5. 2 g of Albidur PU 5640 resin was added to 20 g of PC40UMF resin and stirred at room temperature for 5 minutes to get PUA+4SR solution with PUA:SR equal to 100:4. The resin with and without silicone rubber was then applied on the coupon (with and without silane treatment) using the doctor blade method. The samples were heated to 60°C for 1hr to evaporate the solvent from resin. Subsequent moisture curing (4 h @80 °C with 60% RH) for PU and dual curing (UV curing 20 min, followed by moisture curing 4 h @80 °C with 60% RH) for PUA coating. The average conformal coating thickness on the silane treated coupon was 50 µm.

Adhesion test and chemical characterization

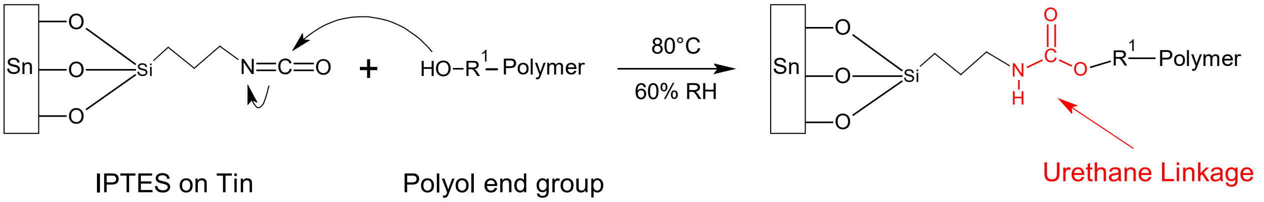
To understand the change in chemical bonds at the interface due to the presence of silane coupling agents, FT-IR (Spectrum100R, PerkinElmer) in an attenuated total reflectance (ATR) mode was performed at the surface of the peeled-side of the coating, separated from Sn surface, for wavenumbers ranging from 600 cm^{-1} to 4000 cm^{-1}. FT-IR (ATR) peaks for PU and PU+5SR coating interface were normalized at 1216 cm^{-1} wavelength (coupled C-N & C-O peak[4]) and for PUA and PUA+4SR coating interface, the data was normalized at 1242 cm^{-1} wavelength (C-O-C peak[13]). Cross-cut tape peel test was used to evaluate the adhesion property of polymeric coatings. Conformal coatings were first applied to the coupon and cut by a blade; whose cut penetrates all the way to the substrate with a lattice pattern of small squares. The adhesive tape was then used to peel off the PU and PUA coatings. To identify the adhesion property of the coating, the delamination percent was calculated based on equation E1.[14,19]

$$\text{Delamination }\% = \frac{\text{Number of peeled-off squares}}{\text{Total number of squares}} \times 100 \qquad \text{(E1)}$$

The average delamination percent out of two samples for each coating was used in this study.

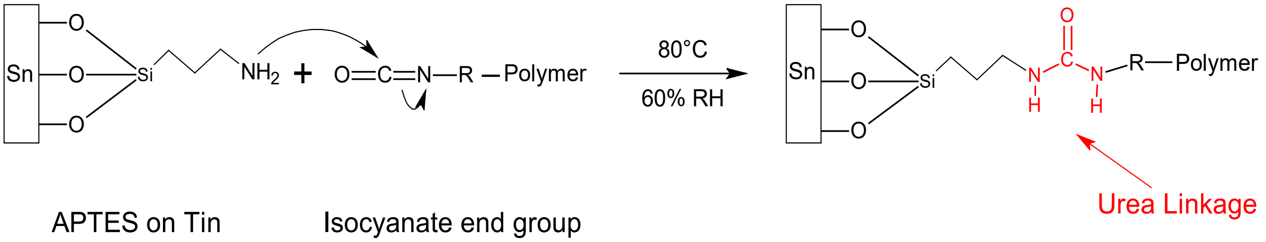
Results and Discussion

The adhesion strength of the thermosetting resin is directly related to the degree of reactivity of the organofunctional group (from silane coupling agent) with the resin.[18] FT-IR peaks between 1790 cm^{-1} and 1390 cm^{-1} provide the intensities of C=O…H-N, CNH and NH bonds at the interface of PU coating and tin surface (with and without silane treatment). It can be seen that the intensity of both the C=O…H-N (1708 cm^{-1}) and CNH peak (1528 cm^{-1}) increased in IPTES silane treatment case when compared to the no silane (NS) case. The proposed reaction between the -NCO group (from IPTES) and polyol (from resin), which result in the formation of urethane bonds at the interface, is shown in the reaction E2.

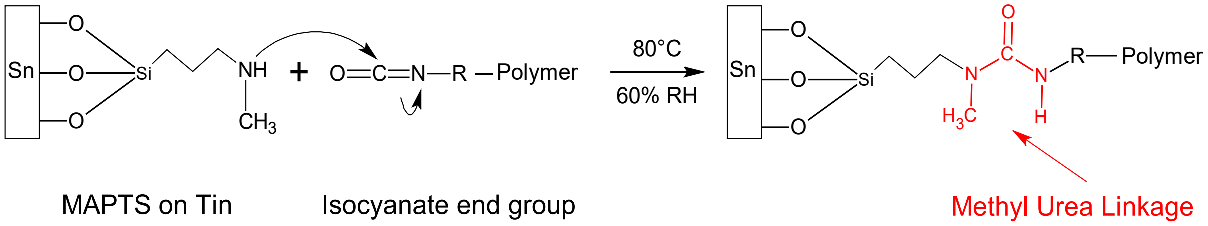


(E2)

The possible reactions between the amine-based silane coupling agent and isocyanate (from resin) is given in the reactions E3 and E4. For APTES silane agent case, C=O bonds (1708 cm^{-1} and 1731 cm^{-1}) have decreased and CNH bond (1528 cm^{-1}) has increased drastically (figure 1a), indicating the possibility of formation of urea linkage at the interface (E3).



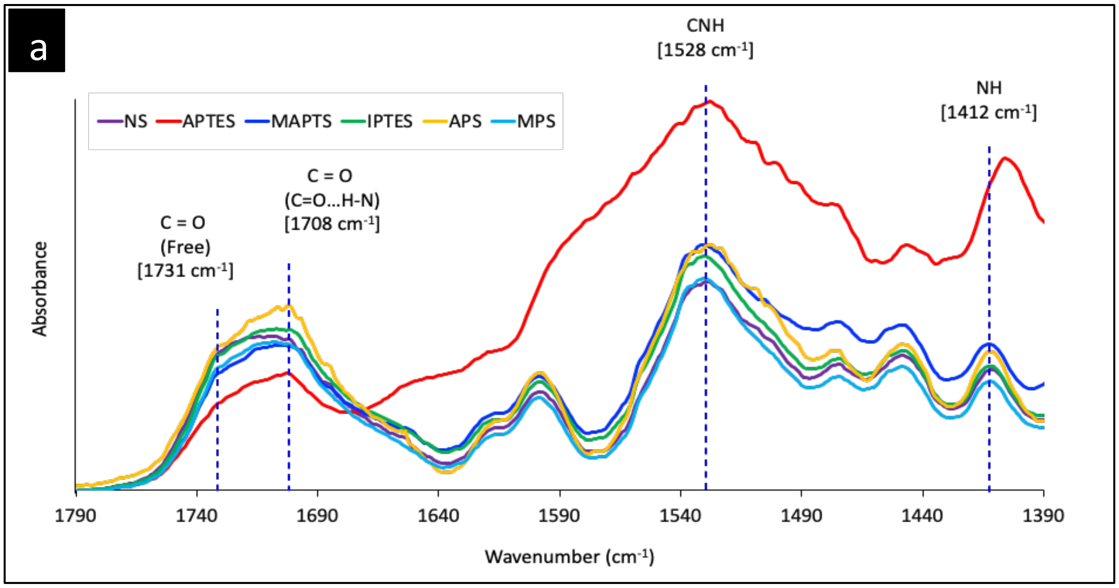
(E3)



(E4)

There was no significant increase of CNH peak at 1528 cm^{-1} for MAPTS silane, indicating no apparent methyl urea linkage formation at the interface. This was because of the higher reactivity of primary amine (APTES) with PU matrix when compared to the secondary amine (MAPTS). Usage of APS and MPS silane agent did not show any link formation with the polyurethane coating. The increase in the C=O peak (1708 cm^{-1}) at the interface belongs to the acrylate bonds. This indicates that the MAPTS, APS and MPS coupling agents did not react with the PU resin.

From figure 1b and c, it is evident that addition of silicone rubber increased the intensity of Si-$(CH_3)_2$ and decreased the intensity of N-H (3297cm^{-1}) and C-H (2869cm^{-1}, 2932cm^{-1} and 2970cm^{-1}) peaks indicating that the increase in silicone rubber decreased the number of urethane bonds at the interface. However, when IPTES silane agent was present, the intensities of N-H and C-H increased with increase in the intensity of Si-$(CH_3)_2$. This was because the -NCO (from silane) reacted with polyol from silicone rubber resin as well as polyol from PU resin, resulting in additional urethane linkage at the interface.



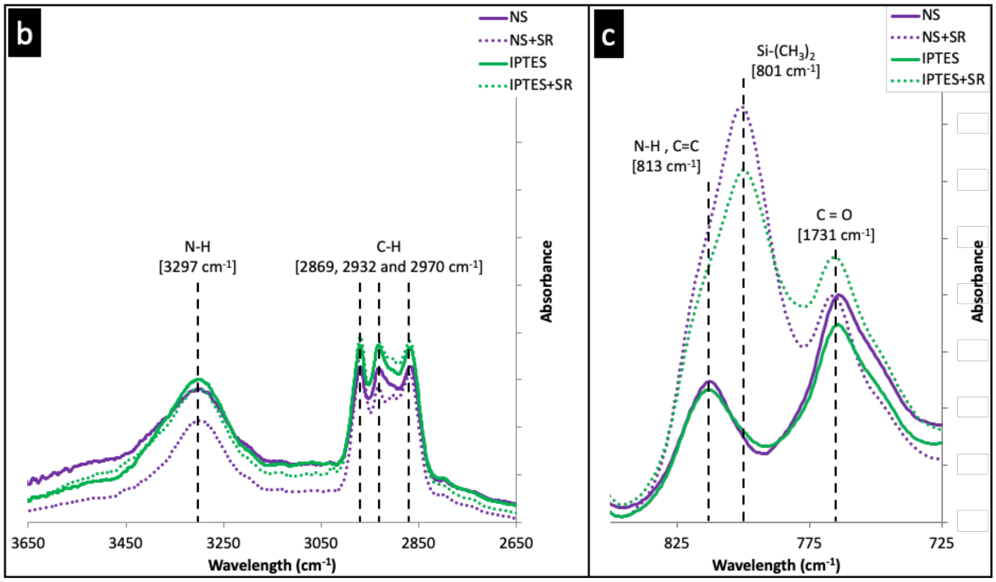
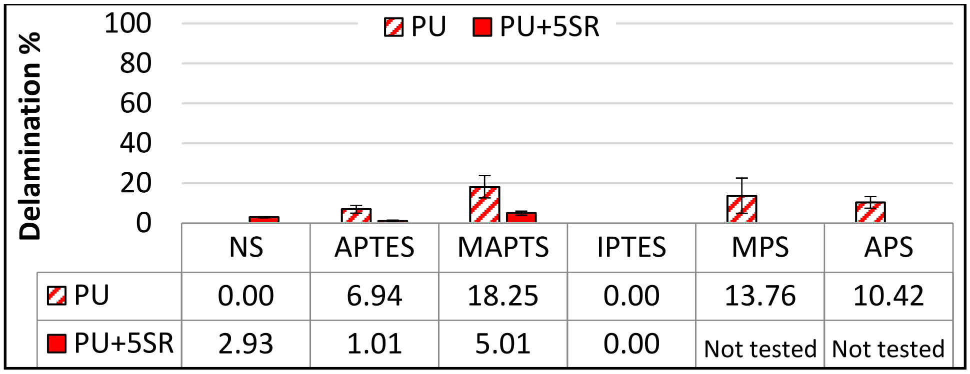


Fig1: FT-IR comparison for PU on different silane treated tin surface between (a) 1790cm^{-1} - 1390 cm^{-1} wavelength; PU vs PU+SR conformal coating on tin surface without silane and IPTES silane treatment between (b) 3650cm^{-1} - 2650 cm^{-1}and (c) 860cm^{-1} - 725 cm^{-1} wavelength

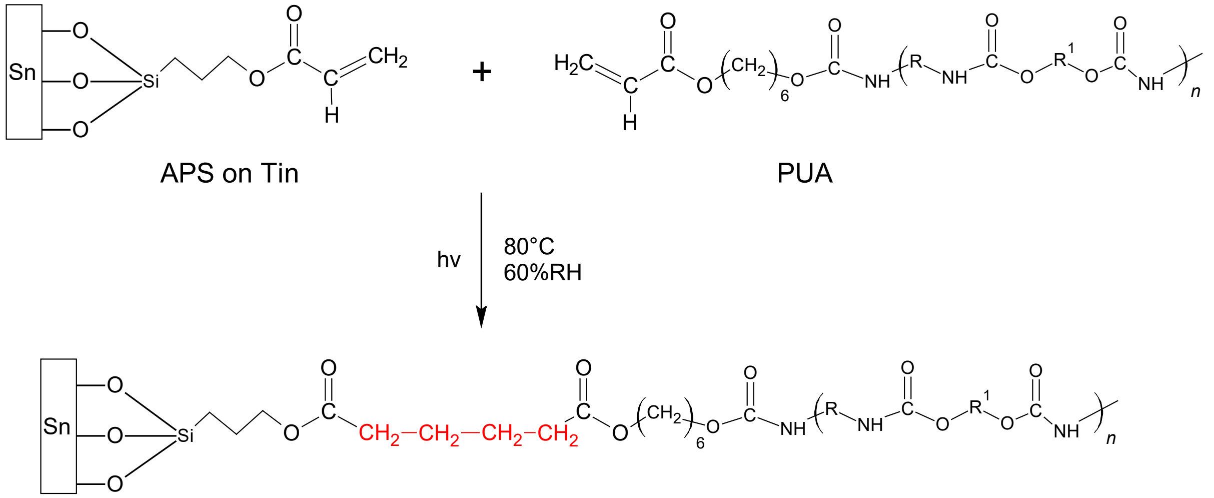
Results from cross-cut tape peel test is given in figure 2. For the PU conformal coating, no silane (NS) condition did not have any delamination; however, addition of silicone rubber to the resin resulted in the delamination percentage of 2.93%. There was no delamination for both PU and PU+5SR coatings when IPTES silane agent was used. This was due to the additional urethane link formed at the interface. Up to 18% of delamination was observed when amine, acrylate and methacrylate-based silane coupling agents were used. It is also seen in figure 2 that the delamination percentage of amine-based silane coupling agent was decreased in PU+SR case. This was because the reaction between the PPG (in silicone rubber resin) and amine (silane agent) provides additional strength at the interface.



	NS	APTES	MAPTS	IPTES	MPS	APS
▨ PU	0.00	6.94	18.25	0.00	13.76	10.42
🟥 PU+5SR	2.93	1.01	5.01	0.00	Not tested	Not tested

Fig 2: Comparison of effect of silane coupling agents on adhesion properties of PU and PU+5SR coatings

FT-IR peaks (1220cm^{-1} - 780 cm^{-1}) of the interface of PUA coating and tin surface, with and without silane treatment, are given in figure 3a. APS silane treatment curve looks similar to the no silane (NS) condition. This indicate that acrylic group at the tail of the APS silane coupling agent might have reacted with the acrylate in the resin, as proposed in reaction E5, forming strong bond during the resin curing.



(E5)

For MPS silane coupling agent, the intensity of C=O peak at 1722 cm^{-1} is decreased while the NH peak at 1457 cm^{-1} is increased and the CNH peak at 1547 cm^{-1} becomes broader (figure 3b), indicating limited reaction at the interface during curing. FT-IR curves show lowered intensity of C-N and C-O-C peaks at 1154 cm^{-1} and 1015 cm^{-1}, respectively, and increased C=O peak for amine and isocyanate-based silane coupling agents. During curing, the amine and isocyanate functional group did not react with acrylate but reacted with isocyanate in the PUA resin. This indicates limited reaction of amine and isocyanate-based silane with the PUA resin. The addition of silicone rubber had a tremendous decrease in the intensities of C-N peak (1154 cm^{-1}) and C-O-C peak (1015 cm^{-1}), as shown in figure 3c, indicating the decrease in the acrylic bonds at the interface due to less acrylate group available at the interface.

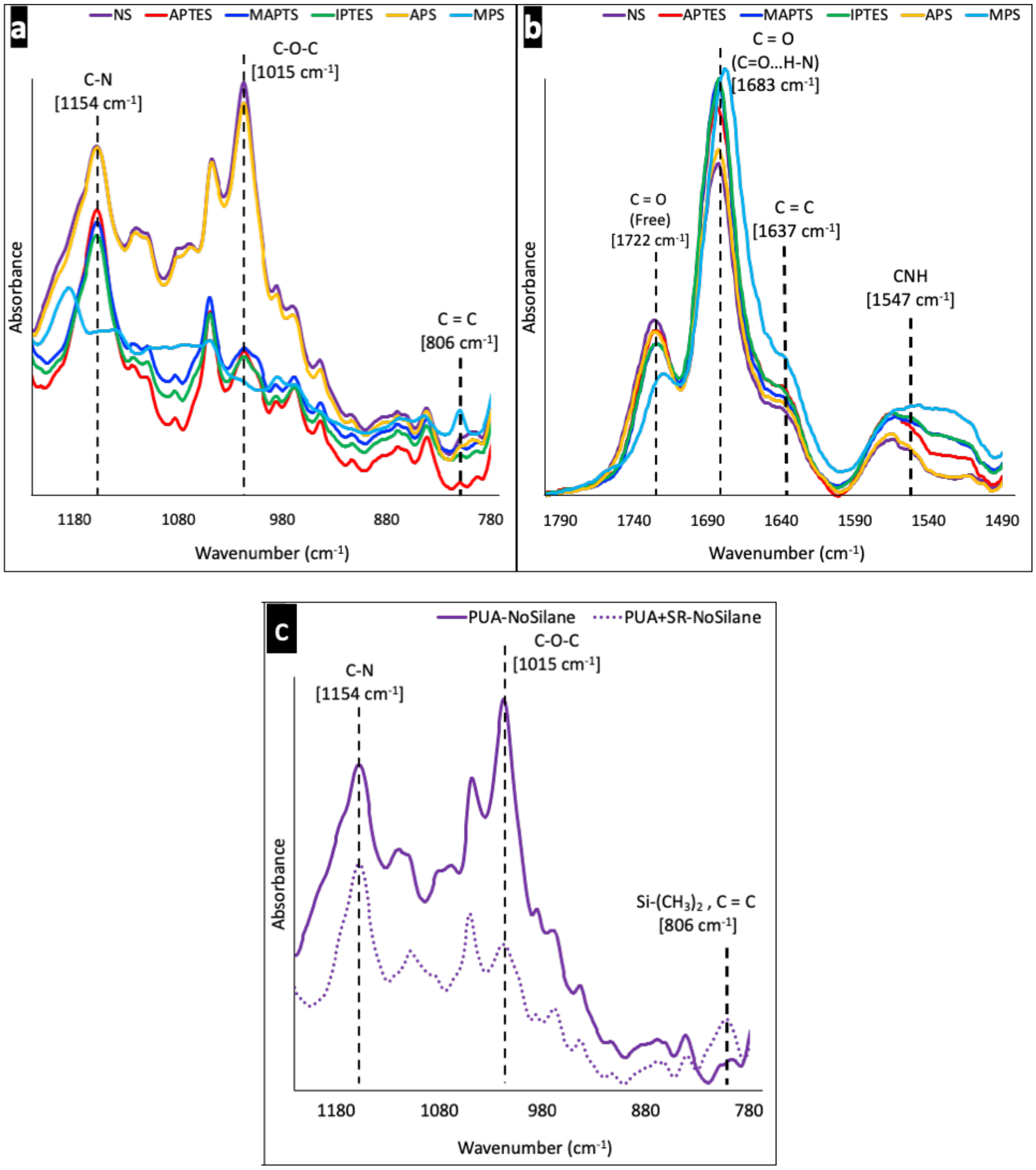
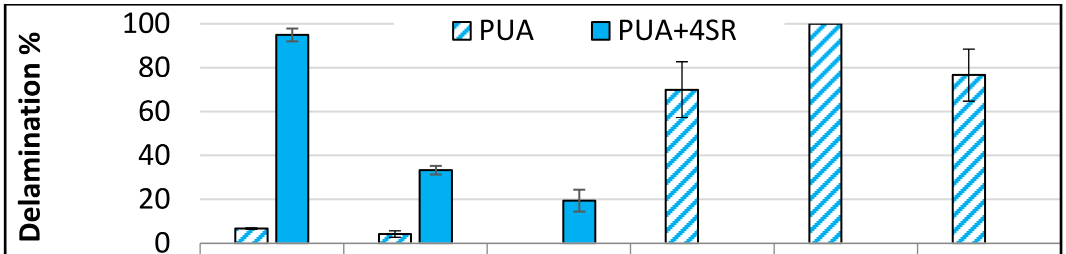


Fig 3: FT-IR comparison for PUA on different silane treated tin surface between (a) 1220cm^{-1} - 780 cm^{-1} wavelength (b) 1790cm^{-1} - 1490 cm^{-1} wavelength and (c)PUA vs PUA+SR conformal coating on tin surface without silane treatment between 1220cm^{-1} - 780 cm^{-1}

PUA coating on tin surface without silane treatment (NS) had a delamination percent of 6.75% (figure 4). There was no delamination during the tape peel test when the tin surface was treated with APS silane coupling agent. The increase in adhesion strength was due to the formation of interfacial bonds, as proposed in E5. Because of limited reactivity (based on FT-IR analysis), MPS showed a little improvement in the adhesion property. When amine-based (APTES and MAPTS) and isocyanate-based (IPTES) agents were used, the adhesion of the PUA coating was very poor.

When silicone rubber was added to the PUA coating, the delamination percent on the no silane treated surface increased to ~95%. When acrylate and methacrylate silane coupling agents were used, the delamination percent was reduced to an average of 19.44% and 33.33%, respectively, indicating the importance of the reactivity between the silane coupling agent and the resin matrix. Silicone rubber particles play an important role in improving toughness of PUA coatings, so it will be essential to optimize the interface chemistry to preserve its adhesion to tin surface.



	NS	MPS	APS	APTES	MAPTS	IPTES
▨ PUA	6.75	4.22	0.00	69.99	100.00	76.63
■ PUA+4SR	94.93	33.33	19.44	Not tested	Not tested	Not tested

Fig 4: Comparison of adhesion properties of PUA and PUA+4SR coatings on tin surface treated with silane coupling agent

Conclusion

PU coating without a silane agent provided excellent adhesion strength. However, addition of silicone rubber to the PU resin decreased the adhesion strength of the coating. While maintaining its adhesion of PU, isocyanate-based silane agent (IPTES) restored the adhesion strength of PU+5SR coating by forming additional urethane linkage at the interface during the curing. In addition, amine-based silane agent (APTES) for PU & PU+5SR coating provided the formation of urea linkage at the interface for strengthening. PUA coating exhibited poorer adhesion than the PU counterpart and the addition of silicone rubber made the PUA coating very susceptible to delamination. Acrylic-based silane agent (APS), this time, provided improved adhesion for PUA, and its effect became significant for PUA+4SR coating that otherwise yielded very poor adhesion. It is attributed to the formation of interfacial bonds that are similar to the bonds in the resin matrix. Methacrylate-based silane agent (MPS) for PUA+4SR coating also contributed to adhesion strength but it seemed to provide limited reaction between the resin and silane.

Silane agents that formed interfacial bonds similar to the resin matrix provided higher adhesion strength than those different from the resin matrix networks. The silane agent that did not form any bonds with the base resin did not improve the adhesion strength of the coating. These cases include amine (MAPTS), acrylic (APS) & methacrylate (MPS)-based silanes for PU coating, and amine (APTES and MAPTS) & isocyanate (IPTES)-based silanes for PUA coating. Hence, this work provides an insight into engineering improved adhesion of the polymeric coating to metal surface by forming the desirable interfacial bonds between the organofunctional group in silane coupling agent and resin matrix.

Acknowledgement

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