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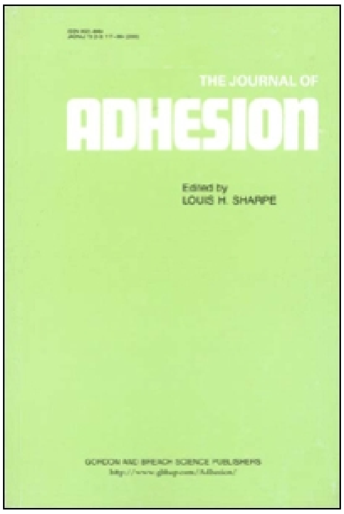

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Atmospheric Pressure Plasma Polymerised Primer to Promote Adhesion of Silicones

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By combining a liquid primer and a plasma jet system, a new route to improved adhesion on various substrates has been developed. The liquid primer is introduced as an aerosol into a plasma jet and the resultant active species are deposited as a polymer coating on adjacent surfaces. Careful control of the plasma parameters produced a dry polymerised coating with functional chemistry designed to enhance the adhesion of silicone sealants to two substrates. This paper describes the surface chemistry and adhesion properties of various coatings on both a plastic and a metal substrate. Selected surface analysis techniques were coupled to both wet and dry adhesion testing to characterise the factors that control adhesion within the system. Mechanical testing indicates that adhesion was improved by several orders of magnitude.

Keywords: Adhesion; Aerosol; Plasma; Primer; Silicone; XPS

1. INTRODUCTION

Improvement of adhesion performance is an ongoing challenge facing silicone adhesive and sealant manufacturers. Traditionally, a variety of adhesion promoters are added to adhesive formulations to enhance adhesion to the substrate. However, these additives can negatively impact product performance, such as cure times, viscosity, clarity, and

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Address correspondence to L.-A. O'Hare, Dow Corning Plasma Solutions, Owenacurra Business Park, Midleton, Co. Cork, Republic of Ireland. E-mail: lesley.ann.ohare@dowcorning.com ultimately the cost of the adhesive. For example, higher cure temperatures and extended cure times are often required to allow the adhesion promoter to migrate to the interface and become effective [1].

Alternatively, the surface of the substrate could be modified in advance of the application of the adhesive to enhance the adhesion. A variety of priming systems have been developed that are applied to the substrate prior to the application of the adhesive. These priming processes often require the use of solvents, drying cycles, careful control of pH, and handling of very reactive primer formulations.

In the past, there have been attempts to enhance the adhesion to various materials using plasma processes. These have typically involved exposing the substrate to a flame or a non-thermal plasma in order to clean and activate the surface [2–4]. This process introduces polar groups on the substrate surface which are capable of forming Si−O−C −C bonds with the adhesive. Such processes can have a limited effective lifetime and adhesion can be unstable when exposed to moisture due to degradation of the hydrolytically unstable Si−O−C bonds. In order to overcome this, some researchers have combined the plasma activation step with the addition of a subsequent wet primer layer [5,6]. However, this results in a multi-step pre-treatment of the sample which is undesirable for commercial application. Other researchers have used plasma polymerisation techniques to deposit primer layers to enhance adhesion. These techniques have typically involved the use of complex vacuum systems and batch processing and have produced primer coatings with only limited control of the deposition chemistry [7,8].

Atmospheric Pressure Plasma Liquid Deposition (APPLD) technology combines atmospheric pressure plasma processing with liquid precursors to deliver highly functional thin-film surface coatings [9,10]. APPLD is a room temperature process that can be applied continuously to substrates in flexible web, rigid sheet, or 3D geometry without the need for solvents or subsequent curing and drying steps.

Using this plasma process, it should be possible to combine the plasma activation step and the chemical primer application into a one-step deposition of a plasma polymerized primer (PPP). This paper investigates if such a PPP can be deposited. The goal of this research is to deposit a PPP layer which is chemically bonded to the substrate and which retains the controlled chemical functionality of the precursor molecules. Due to the chemistry control of APPLD and the wide range of available liquid precursors available [11], the chemistry of the PPP can be tailored to allow the primer to participate in the adhesive cure reactions. This should create a primer that is bonded to both the adhesive and the substrate resulting in excellent wet and dry adhesion of the adhesive to the substrate, as shown schematically in Figure 1.

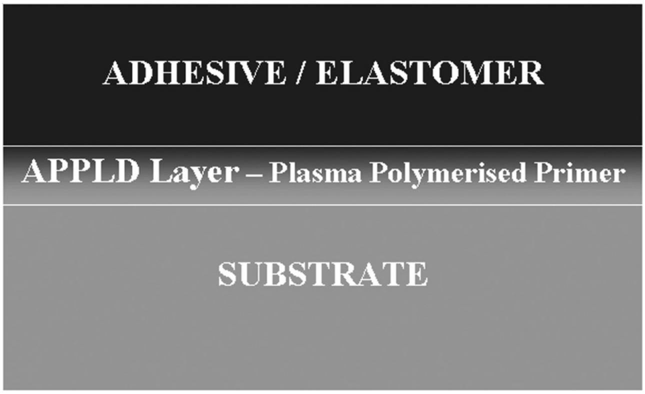


FIGURE 1 Schematic of plasma polymerised primer.

A series of experiments were undertaken to study the adhesion of a hydrosilylation curable liquid silicone rubber (LSR) to plastic and metal components. The PPP was deposited using a proprietary non-thermal plasma jet system, Dow Corning® SE-2000 PlasmaStream (Figure 2) with an integrated aerosol delivery system for introduction of the liquid primer precursor (DowCorning, Midleton, Cork, Ireland). The plasma jet system was mounted on a computer numerically controlled (CNC) XYZ table and scanned over the surface of the substrate while the liquid precursor was introduced to form a thin coating on the

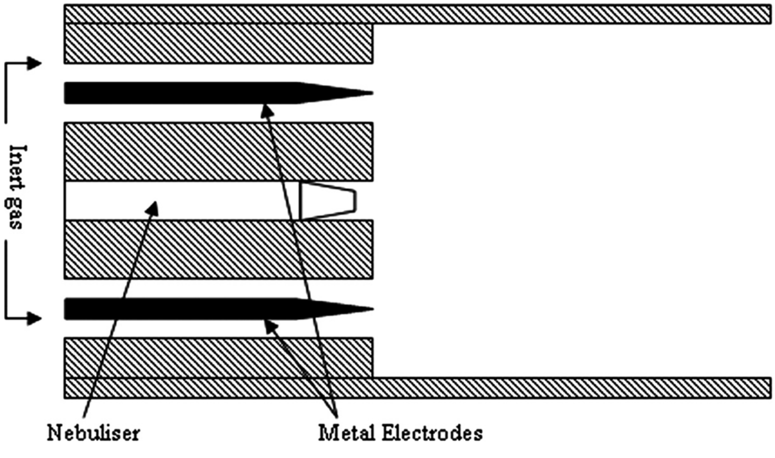


FIGURE 2 Schematic of Dow Corning SE-2000 PlasmaStream—non-thermal plasma jet with liquid precursor delivery.

surface of the substrate, which is expected to be of nanometre thickness [12]. The plasma jet performs two roles; it delivers the liquid precursor in aerosol form to the substrate surface and it activates the substrate surface and the liquid precursor with free radicals and ions which initiate reactions between the two.

2. EXPERIMENTAL

2.1. Precursors

The liquid precursor chosen was a mixture of Dow Corning MH-1107 fluid (polymethylhydrogen Siloxane—MW ~ 3000) supplied by Dow Corning (Barry, UK) and tetraethylorthosilicate (TEOS) supplied by Sigma Aldrich (Dublin, Ireland). The structures of these chemicals are shown in Figure 3. The Dow Corning MH-1107 fluid possessed the necessary Si–H chemical functionality to participate in the hydrosilylation cure of the LSR. It is also expected to provide a flexible component to the primer coating. The TEOS component was chosen to provide condensation cross-linkable chemistry useful for bonding to hydroxyl surfaces. TEOS condensation would also be expected to yield a highly resinous structure that is essential to the formation of a coherent, highly cross-linked, and stable PPP coating.

2.2. Substrates

The polybutyl terephthalate (PBT) substrate used was Celenex 3300 D, which is 30% glass filled (Ticona, Telford, UK); the 304 stainless steel substrate was supplied by Q Lab Corporation (Manchester, UK). Both substrates were used "as received." No additional cleaning steps were carried out prior to deposition. A small concentration of silicon was detected on the PBT substrate prior to any treatment. Two samples of each were used, with the adhesion results presented being the average.

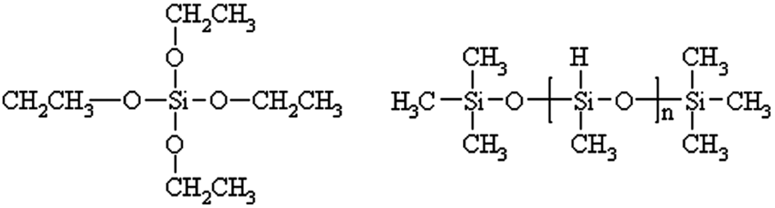


FIGURE 3 Chemical structure of TEOS (left) and MH 1107 (right).

2.3. Primer Deposition

A 1/2 factorial, (2^{4-1}) experimental design was undertaken to determine the effect of the plasma process on the adhesion of the LSR to PBT and 304 stainless steel. The factors varied were plasma power, CNC line speed, precursor liquid flow rate, and the TEOS/Dow Corning MH-1107 ratio. Statistical analysis of the experimental results was carried out using Stat-Ease Design Expert 6.0.5 software (Stat-Ease, Inc., Minneapolis, MN, USA).

Coatings were deposited in a helium flow of 7 standard litres per minute (slm). The plasma was generated by applying AC voltage to metallic electrodes at a frequency between 10 and 20 kHz with an output voltage of 20–25 kV peak to peak. The process conditions used in the preparation of each sample are summarised in Table 1.

2.4. Adhesion Testing

Following deposition of the PPP coating on the substrates, hydrosilylation cured LSR (Silastic® 9280/50) was applied manually to each PBT and 304 stainless steel sample and cured at 150°C for 20 minutes. The substrate dimensions were 70 × 25 mm with thicknesses of 7 and 1 mm for the PBT and stainless steel, respectively. The LSR was applied in two layers of 2 mm thickness covering the entire surface of the substrate. A 100 mesh stainless steel cloth was placed on the first layer of LSR before applying the second layer of LSR. The sample was prepared for peel testing by cutting through the LSR and wire mesh along the length of the sample yielding a 13 mm wide strip suitable for peeling. To facilitate crack growth near the substrate surface, a pre-cut through the first layer of LSR was made along the face of the peel strip

TABLE 1 Process Parameters for PPP Deposition Experiments

Sample #	Plasma power (W)	Liquid flow (μl/min)	CNC speed (mm/sec)	% TEOS
1	low	15	25	25
2	high	15	10	25
3	high	5	25	25
4	low	5	10	25
5	low	5	25	75
6	high	15	25	75
7	Low	15	10	75
8	High	5	10	75
Plasma only	High	–	10	–
Control	–	–	–	–

before the adhesion test was started. Both a dry peel test and a wet creep peel test were utilised to determine adhesion strength. Dry adhesion testing was carried out using a simple 180° peel test control according to ASTM C784–80. The wire mesh was pulled at 50.8 mm per minute. The wet peel testing was performed in a custom built creep frame. This consists of a water bath and lever arms to apply a constant load to the peel specimens while simultaneously submerged in 37°C water. The details of this device are described elsewhere [13]. The crack speed was measured while under a load of 330 N/m at a 45° peeling angle, unless otherwise stated in the text. The locus of failure was assessed visually, and determined to be either interfacial or cohesive. The results of dry peel force and wet peel testing of the LSR applied to PPP treated PBT substrates are shown in Table 2.

2.5. X-Ray Photoelectron Spectroscopy

XPS was carried out on a Kratos Analytical Axis Ultra spectrometer (Kratos Analytical, Manchester, UK). The instrument is equipped with a spherical mirror analyser (165 mm mean radius hemispherical analyser), an integral automatic charge neutralizer, and a magnetic lens. A monochromated aluminium (Al Kα) X-ray source was used to record spectra at normal emission. A nominal power of 300 W (15 mA emission current, 20 kV anode potential) was used for all samples. A pass energy of 160 eV was used to capture wide area scans, whilst 20 eV was used to obtain the high resolution core level spectra. All of the samples of interest required charge neutralisation. Elemental

TABLE 2 Analysis Results from LSR-PPP-PBT Samples

Sample #	WCA (°) St Dev 5%	Dry peel force (N/m) st dev 15%, 25 mm/min	Failure mode	Wet crack speed (mm/s) st dev 5% 35°C, 330 N/m	Failure mode
001	99	1897	Cohesive	3.5×10^{-5}	Cohesive
002	102	2005	Cohesive	3.6×10^{-5}	Cohesive
003	98	771	Cohesive	1.4×10^{-1}	Interfacial
004	100	276	Mixed	9.9×10^{-1}	Interfacial
005	87	157	Interfacial	1.0	Interfacial
006	91	315	Cohesive	5.0×10^{-4}	Cohesive
007	92	894	Cohesive	5.0×10^{-5}	Cohesive
008	87	196	Interfacial	3.0	Interfacial
Plasma only	38	50	Interfacial	5.0	Interfacial
Control	75	46	Interfacial	5.0	Interfacial

composition data presented is the average of three analyses within a 1×1 cm sample.

2.6. Contact Angle Analysis

Contact angle analysis was carried out on a CAM2000 Optical Contact Angle Meter (KSV, Finland). Equilibrium contact angle measurements were performed using 2.5 µl drops of HPLC grade water as the probe liquid. The image was captured 30 seconds after the drop was placed on the film. The left- and right-angles of three drops were measured, with the reported value being an average value of these (θ_{Water}).

3. RESULTS AND DISCUSSION

3.1. Adhesion to PBT

In the absence of any primer, there was negligible adhesion of the LSR to the substrate and the LSR peeled off with minimal force. In all cases the application of the PPP improved the dry adhesion strength of LSR to PBT. However, activation or cleaning of the PBT surface with plasma containing no liquid precursor did not significantly improve adhesion. This indicates that it is the deposition of the primer layer, not merely changes in surface energy or the introduction of polar species, which led to enhanced adhesion. Furthermore, since identical plasma conditions were used for the comparison of activation *versus* deposition, this suggests that any enhanced roughening of the surface can be negated as a significant factor in the mechanisms of adhesion for the PBT samples. Statistical analysis of the dry peel strength data indicated that the liquid flow and the precursor mixture strongly influence the coating adhesion under dry conditions. Decreasing the TEOS concentration in the precursor mix and increasing the flow of precursor liquid increased the adhesion strength. For the wet creep peel test, the use of a high precursor flow rate was found to have the most statistically appreciable effect on coating adhesion. All of the samples prepared with high precursor flow rate exhibited cohesive failure in the LSR under wet testing conditions.

A higher precursor flow and a higher concentration of MH-1107 fluid in the precursor should lead to a higher concentration of Si–H functionality on the surface of the PBT and this may be expected to lead to increased bonding to the LSR during the cure cycle. This was further investigated using a combination of XPS and water contact angle (WCA) analysis.

Previous experiments have shown that under identical process conditions TEOS can be used to deposit hydrophilic plasma coatings (WCA values in the range 23–56°), while Si$-$CH$_3$ functional siloxanes such as MH 1107 produce coatings with high water contact angle values (WCA values greater than 100°) [12]. All of the precursor primer formulations produced WCA values that were in the range 87–102° (Table 2). MH 1107-rich formulations produced approximately 10° higher WCA than the TEOS-rich precursor derived coatings. However, all coatings produced WCA values greater than would be expected from a TEOS rich surface and this suggests that preferential segregation of the MH 1107 component to the surface may be occurring. The thermodynamically driven migration of methyl-rich siloxanes to the surface of such plasma coatings have been reported previously [12,14,15]. XPS analysis was used to confirm this observation and to determine the chemistry of the deposited coatings, using a method described elsewhere [16]. For ease of representation, the silicon chemistry has been denoted by the letters M (mono) [$(CH_3)_3SiO_{1/2}$], D (di) [$(CH_3)_2SiO_{2/2}$], T (tri) [$(CH_3)SiO_{3/2}$], and Q (quaternary) [$SiO_{4/2}$], indicating the number of oxygen atoms attached to the silicon.

3.2. XPS Analysis of Coatings on PBT

3.2.1. Elemental Composition

The elemental composition of the as received PBT surface and after activation of the PBT surface with plasma containing no liquid precursor are shown in Table 3. The plasma activation of the PBT caused an increase in the oxygen concentration at the surface. This is in accord with the decrease in WCA observed after plasma activation. It was also observed that the silicon concentration increased after plasma activation.

The elemental composition of each coating as determined by XPS is presented in Table 3. Comparison of the experimental composition for the TEOS-rich coatings (Samples 5–8) with the theoretical stoichiometric composition indicates that a lower carbon concentration was detected. However, the carbon concentration was higher than expected from a 100% TEOS coating and was closer to the experimental values observed for a 100% MH 1107 coating. As XPS is a surface sensitive technique, this suggests that the methyl-rich MH 1107 component is segregating preferentially to the surface, in agreement with the WCA results. It is also proposed that the same surface segregation effect may also be occurring in the 25% TEOS coatings (Samples 1–4), although it is not possible to confirm this from only elemental composition data.

TABLE 3 Elemental Composition of Plasma Polymerised Primer Containing TEOS and MH 1107 Deposited on PBT

	Relative concentration (atomic %)		
Sample identifier	Oxygen	Carbon	Silicon
Stoichiometric 100% MH 1107	32	35	33
Experimental 100% MH 1107	40 ± 3.6	41 ± 4.7	19 ± 2.3
100% TEOS	31	61	8
Experimental 100% TEOS	48 ± 4.8	23 ± 5.2	28 ± 0.3
Stoichiometric 25% TEOS mix	32	43	25
1	40 ± 0.4	38 ± 0.2	23 ± 0.6
2	45 ± 0.5	32 ± 0.8	23 ± 0.4
3	47 ± 2.0	30 ± 1.2	23 ± 0.7
4	47 ± 0.2	28 ± 0.3	25 ± 0.0
Stoichiometric 75% TEOS mix	31	56	13
5	36 ± 0.4	38 ± 0.6	26 ± 0.3
6	41 ± 0.8	37 ± 0.8	22 ± 0.4
7	40 ± 0.9	36 ± 0.6	24 ± 0.7
8	47 ± 0.9	29 ± 0.7	24 ± 0.3
Plasma only	32 ± 2.7	61 ± 2.8	4 ± 2.3
Control	21 ± 1.7	76 ± 3.0	2 ± 0.7

Variations in the oxygen concentration, with corresponding changes in the carbon concentration were detected, and were found to be related to the plasma parameters. Samples treated at low power and with a high precursor flow rate (Samples 1 and 7) exhibited similar oxygen concentrations, which were lower than the majority of the samples. Conversely, samples prepared with high power and low precursor flow rate were found to have higher oxygen concentrations (Samples 3 and 8). These observations can be readily related to the power delivered (W) and the flow of the precursor (F_m), as per the plasma polymerisation model developed by Yasuda and Hirotsu [17].

The increased oxidation present in these coatings can be explained by cleavage of the Si–H bond in MH 1107, followed by cross-linking through an Si–O–Si linkage. Additionally, oxidation or removal of the methyl group on this molecule will also be occurring. These are both known mechanisms of siloxane modification initiated by UV radiation and corona treatment [18]. This will be confirmed by examination of the curve-fits for the C 1s and Si 2p core levels, where an increase in silicon oxidation state would be observed. Furthermore, removal of the ethyl groups associated with the TEOS molecule would also result in an apparent decrease in carbon and increase in oxygen as shown in Table 3. However, it will not be possible to confirm the reaction mechanism of TEOS through interpretation of the Si 2p core level, since the Si atom is in the "Q" siloxy environment in either case.

3.2.2. Core Level Spectra

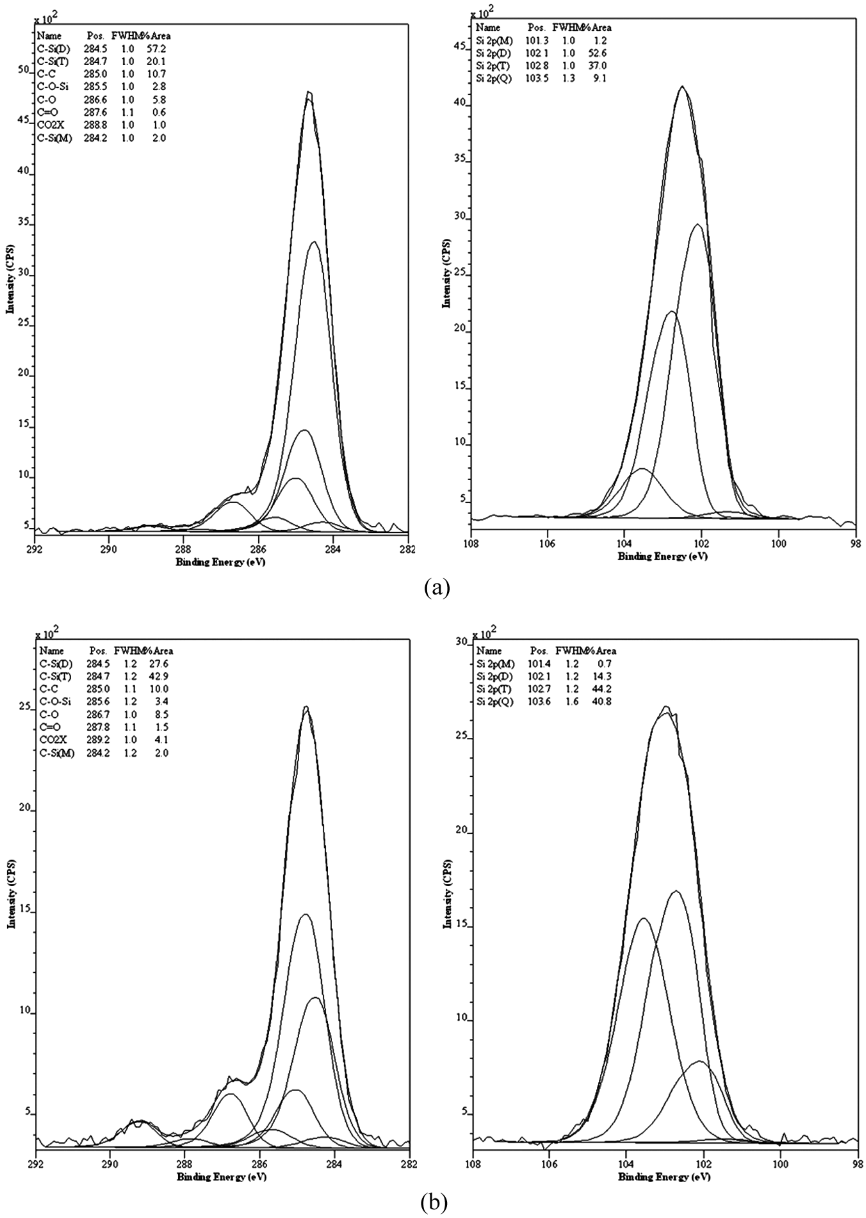
The Si 2p core level spectra acquired from the as received PBT indicate that between 80 and 90% of the silicon present was in the "M" siloxy environment, and the remaining silicon present at the surface was in the Q siloxy environment. The Si 2p core level spectra acquired from the PBT surface after activation with plasma containing no liquid precursor showed a reduction in the amount of silicon present in the M siloxy environment and an increase in the amount of silicon in the Q siloxy environment. This could be due to the plasma converting the M type silicon to Q type silicon or due to ablation of the surface by the plasma to expose the glass present in the PBT.

The C 1s core level spectra acquired from the PBT surface, after activation with plasma containing no liquid precursor, indicated that chain scission of the PBT was occurring. This was interpreted by the need to add peaks representative of carboxylic acid functionality, which is consistent with cleavage of the ester bond. The increase in amount of Q type silicon and the presence of carboxylic acid functional groups at the surface of the PBT after plasma activation is consistent with a reduction in WCA. However, the adhesion data show that the changes in surface chemistry from treatment with plasma containing no liquid precursor did not make any significant difference to the adhesion of LSR to the PBT.

The curve-fitted C 1s and Si 2p core levels for Samples 1 and 3 are compared in Figure 4. The variations in the centroid of the Si 2p core level are clear: for Sample 3 (high W/F_m) the peak maximum is at a higher binding energy, indicating that the coating has a higher concentration of highly oxidised siloxy species when compared with Sample 1.

Additionally, differences are also apparent in the oxidation states of carbon. For Sample 1 (low W/F_m) there is little oxidation and only limited C–O species are detected. However, for Sample 3, the intensity of the component assigned to C–O is significantly enhanced and a component assigned to COOX was also required to ensure a good fit to the experimental data.

When the curve-fits for samples deposited from a mixture of 75% TEOS and 25% MH 1107 are examined (Figure 5), similar observations can be made related to the oxidation state of both silicon and carbon. As with the TEOS-rich samples, the oxidation states of the MH-1107-rich plasma coatings can be controlled by altering the energy delivered per molecule of precursor.



(a)

(b)

FIGURE 4 Curve-fits for carbon (C 1s) and silicon (Si 2p) core levels of plasma polymerised primer containing 25% TEOS and 75% MH 1107 deposited on PBT. (a) Sample 001—low energy per molecule, (b) sample 003—high energy per molecule.

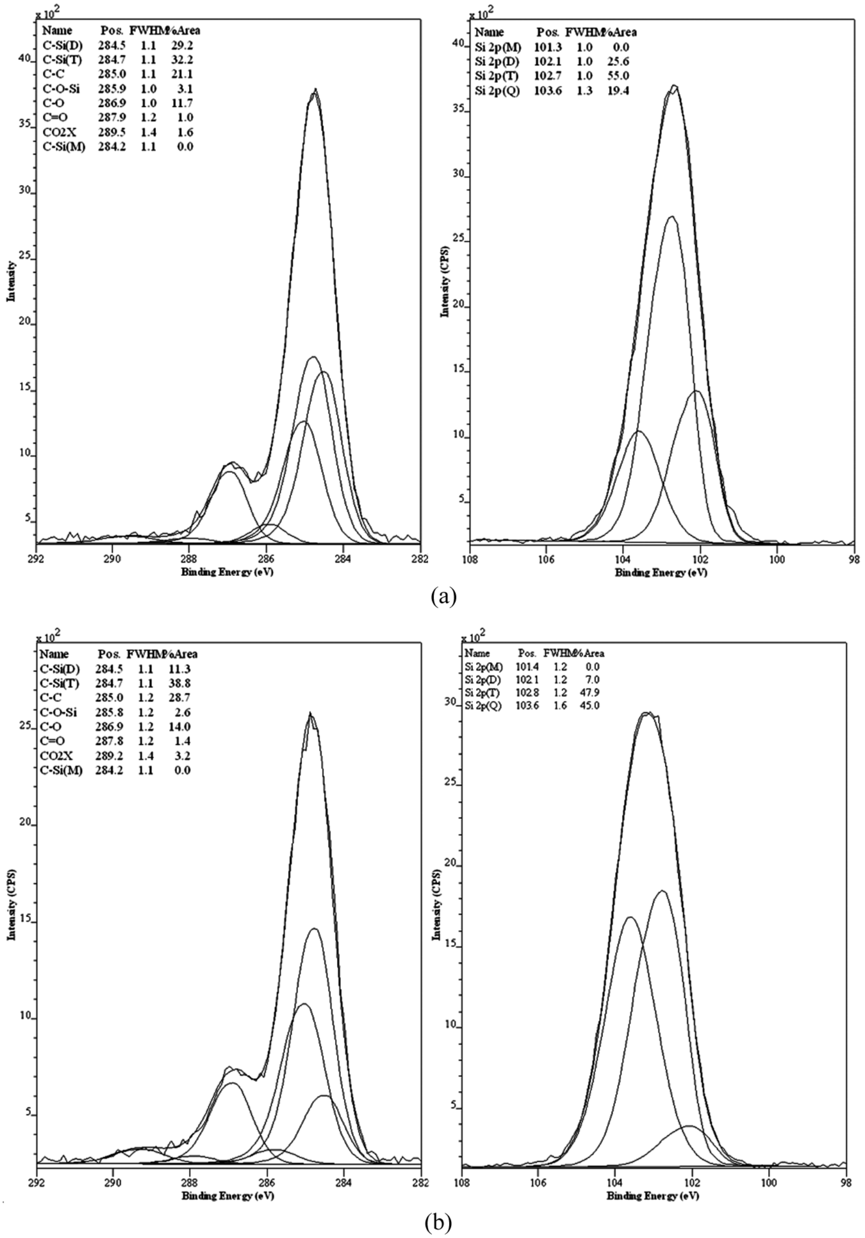


FIGURE 5 Curve-fits for carbon (C 1s) and silicon (Si 2p) core levels of plasma polymerised primer containing 75% TEOS and 25% MH 1107 deposited on PBT. (a) Sample 005—low energy per molecule, (b) Sample 008—high energy per molecule.

TABLE 4 Siloxy Environment for Plasma Polymerised Primer Coatings Deposited from TEOS and MH 1107 on PBT Substrate

	Relative concentration (% of Si 2p peak)			
Sample identifier	Si $2p^{M}$	Si $2p^{D}$	Si $2p^{T}$	Si $2p^{Q}$
Stoichiometric 100% MH 1107	4	96	0	0
Experimental 100% MH 1107	0.1	4.4	30.8	64.7
Stoichiometric 100% TEOS	0	0	0	100
Experimental 100% TEOS	0	0	30	70
Stoichiometric 25% TEOS	4	88	0	9
1	1	53	37	9
2	1	31	42	26
3	1	14	44	41
4	0	18	44	38
Stoichiometric 75% TEOS	2	51	0	47
5	1	31	51	18
6	0	15	51	34
7	0	26	55	20
8	0	7	48	45
Plasma only	21	0	0	79
Control	86	0	0	14

The siloxy environments for all samples are summarised in Table 4. As proposed previously, formation of Si–O–Si linkages is occurring during the deposition process. This is seen by the generation of "T" and Q siloxy species, and a reduction in the concentration of "D" siloxy species compared with the theoretical stoichiometric values.

3.3. Adhesion to Steel

The plasma polymerised primer deposition on 304 stainless steel substrates was varied using identical conditions to those employed during the PBT deposition experiments (Table 1). Dry peel testing clearly showed that the blank sample (no primer) failed easily, but all other samples were found to exhibit excellent adhesion and the dry peel test could not differentiate between the samples. Unfortunately, a plasma-only test condition was not prepared for the stainless steel substrate.

Therefore, the analysis was focused on the wet creep test results. Again, the blank was found to exhibit rapid failure, but all of the PPP samples exhibited excellent adhesion and minimal crack formation (10^{-5} mm/sec crack speed) at 37°C & 330 N/m. Therefore, a more stringent test was carried out using hotter water (60°C) and greater

TABLE 5 Adhesion Test Results from LSR-PPP-Stainless Steel Samples

Sample #	WCA (°) St Dev 4.5%	Dry peel force (N/m) st dev 15%, 25 mm/min	Failure mode	Wet crack speed (mm/s) st dev 5%, 60°C, 550 N/m	Failure mode
001	107	2490	Cohesive	3.5×10^{-4}	Mixed mode
002	103	2730	Cohesive	3.6×10^{-4}	Mixed mode
003	111	2370	Cohesive	5.0×10^{-4}	Mixed mode
004	110	2656	Cohesive	4.9×10^{-5}	Mixed mode
005	107	2988	Cohesive	5.0×10^{-5}	Mixed mode
006	112	2667	Cohesive	4.6×10^{-5}	Mixed mode
007	109	1992	Cohesive	8.6×10^{-5}	Mixed mode
008	109	2324	Cohesive	5.4×10^{-5}	Mixed mode
Control		85	Interfacial	5	Interfacial

force (550 N/m). Results of this test and the aforementioned dry testing are shown in Table 5.

The samples were all found to exhibit very high adhesion strength and crack speeds were consequently low. Statistical analysis of these results indicated that the precursor formulation had the most significant impact upon the test results. Contrary to the effect seen on the PBT substrates, a higher concentration of TEOS in the PPP contributed to better adhesion of LSR to steel. This effect may be due to the different surface chemistry that is present on each substrate surface. TEOS is known to provide excellent adhesion to metals due to condensation reactions between the Si–OEt group and hydroxyl species present on the metal surface [1]. As with the earlier PBT samples, water contact angle measurements of the plasma coatings indicate that the MH 1107 component has segregated to the surface for all these samples, as indicated by all samples producing a contact angle in excess of 100° (Table 5). As the outer surface has sufficient MH 1107 (Si–H functionality) content to bind to the LSR in all the samples, the adhesion may be controlled by the bond between the steel and the primer layer. Consequently, the higher TEOS concentrations in some formulations should enhance bonding to the steel surface to produce the optimum adhesion results observed for the higher TEOS formulations.

4. CONCLUSIONS

In conclusion, a tailored plasma polymerized primer (PPP) was deposited onto PBT and stainless steel substrates in order to improve the adhesion of a hydrosilylation cure LSR adhesive. Dry peel tests showed that PPP can provide significant improvement in adhesion with samples only failing cohesively in the LSR. Plasma treatment without liquid precursor did not significantly improve adhesion for the PBT substrate. Testing using a wet crack speed measurement further confirmed that the primer provided significant improvements in adhesion. Under wet loading, many of the samples were found to exhibit several orders of magnitude improvement in adhesion over the non-plasma treated sample. The surface chemistry of the primer layer appears key to the adhesion control.

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