Metal-Plastic Adhesion in Injection-Molded Hybrids

Mari Honkanen[1], Maija Hoikkanen[2], Minnamari Vippola[1], Jyrki Vuorinen[2] and Toivo Lepistö[1]

[1]Laboratory of Materials Characterization and [2]Laboratory of Plastics and Elastomer Technology, Department of Materials Science, Tampere University of Technology, P.O.B. 589, FIN-33101 TAMPERE, Finland

Corresponding author:	Mari Honkanen
Address:	Tampere University of Technology, Department of Materials Science, P.O.B. 589, FIN-33101 Tampere, Finland
Email:	mari.honkanen@tut.fi
Telephone:	+358408490133
Fax:	+358331152330

ABSTRACT

Polymer-metal hybrids are replacing steel structures in many applications. Combining metals and plastics is, however, complicated because they have very different physical and chemical characteristics. This study characterizes plastic-metal adhesion in insert-injection-molded hybrids. Diaminofunctional silane was used as coupling agent between thermoplastic urethane and stainless steel. Before silane treatment, various surface treatments, including electrolytic polishing, and different oxidation treatments, were used for steel inserts to understand better the bonding between silane and steel. The effects of the surface treatments and silane application on plastic-metal adhesion were studied by means of contact angle measurements, adhesion tests, and microscopic characterizations. Electrolytic polishing and oxidation of the steel inserts improved significantly silane bonding to the steel insert, and, consequently, plastic adhesion to steel.

Keywords: Plastic-metal hybrid; Plastic-metal adhesion; Insert-injection molding; Silane coupling agent; Scanning electron microscopy; Peel test

1. INTRODUCTION

Preparation of plastic-metal hybrids by insert injection molding offers an interesting manufacturing route for multi-functional components in a few processing steps. Hybrid parts can offer, e.g., savings in cost and weight, consolidation of parts, better dimensional stability, high component integration, and faster assembly due to fewer parts. Versatile plastic-metal hybrids can be used in several applications, such as computers, electronics, automotive, and aircraft industries [1-4]. Currently, plastic-metal hybrids are, e.g., replacing metal structures in the front-end modules of cars [5].

Metals and plastics differ greatly in their physical and chemical characteristics. This difference usually causes poor adhesion between a metal insert and plastic, shrinkage of plastic, residual stresses and hence bending of the hybrid. In current industrial hybrid applications, adhesion is usually based on pre-heating or perforating the insert or tightening the plastic around the insert. In many applications planar inserts are needed, but a detailed knowledge of the adhesion between metal and plastic is still lacking [1,2,6].

Coupling agents are chemicals that improve adhesion between two or more dissimilar constituents such as plastic and metal. Silanes are the most commonly used coupling agents to bond organic materials to metals or metal oxides and have now replaced chromium complexes. In addition, titanates and zirconates are also used as coupling agents [7].

In the plastics industry, the most common organofunctional silanes have a typical structure given in equation (1):

$$(RO)_3SiCH_2CH_2CH_2\text{-}X \qquad (1)$$

where RO is a hydrolysable group and X is an organofunctional group [8].

Silanes can form strong bonds with both metals and polymers. During silane treatment, alkoxy groups on silicon hydrolyze resulting in silanols after addition of water or because of residual water on the metal surface. Afterwards, silanols react with metal hydroxyl groups to form stable and covalent oxane bonds (Si-O-metal). Silane films are cured to ensure condensation - during curing, silane molecules react with each other on the metal surface, resulting in a network structure. Hydrolysis and condensation reactions of alkoxysilane and its bonding to an inorganic surface are shown in Fig. 1. Silane bonding with polymers is complex, and the reactivity and solubility of polymers should match those of silane used [9-13].

Classically it is assumed that silanes arrange themselves perpendicular to the metal surface. The surface topography influences the arrangement; a rough surface may disrupt the order of the first silane layer preventing the formation of the second. Thus, smooth surfaces are the best substrates for silane bonding [14]. The optimum thickness of a silane layer is estimated to be from 0.5 to 10 mm in polypropylene-aluminum hybrid [9]. With thinner or thicker layers, adhesion will suffer but the optimum thickness depends on the bonded materials.

Modification of the metal surface can affect significantly the bonding of silane to the metal surface. Susac et al. [15] studied the bonding of organosilane on aluminum alloy. Mechanically polished fresh and 20 hours air-exposed samples were used in their silane treatments. They noticed that silane bound poorly to a fresh, polished sample, and that the existence of Al-Cu-Mg and Al-Fe-Cu-Mn-Si particles affected the adhesion as the silane bound to the matrix but not to the particles. Silane bound much better to an air-exposed than a fresh sample, and its bonding to the air-exposed samples was strongly affected by the presence of Al-Cu-Mg and Al-Fe-Cu-Mn-Si particles [15].

Kim et al. [16] studied the bonding of two organosilanes on aluminum alloy. They also studied the effect of oxidation treatment of aluminum on silane bonding. Samples were mechanically polished and then exposed to air for 20 hours or oxidized in air at 200°C for 15 minutes. In the air-exposed samples, both the presence of Al-Cu-Mg and Al-Fe-Cu-Mn-Si particles and matrix affected bonding, as in Susac et al. studies. During oxidation treatment at 200°C, oxides grew on the aluminum surface, and a uniform silane layer formed on the oxide layer of aluminum [16].

The aim of this study was to characterize the adhesion between plastic and metal in insert-injection-molded hybrid parts. The approach is based on the well-known and largely studied coupling properties of organofunctional silanes. To our knowledge, only one previous reference [17] considers the use of silanes in insert-injection-molding and it is mainly focused on polymer/silane interfaces. The approach considered in this study consists in the use of aminofunctional silane as coupling agent between thermoplastic urethane and stainless steel. This is also the first publication, to our best knowledge, on the plastic-silane-metal cross-sections studied by scanning electron microscopy. In this study, before silane treatment, planar steel inserts were surface-treated in various ways to achieve a better bonding between silane and insert and thus between plastic and steel. The effects of the surface treatments and coupling agent on plastic-metal adhesion were studied by means of contact angle measurements, microscopic characterizations, and adhesion tests.

2. EXPERIMENTAL

2.1. Materials

The insert material was stainless steel 4301 from Outokumpu Tornio Works, Finland; its chemical composition and nomenclature are given in Table 1. The as-received steel plate was cold-rolled, heat-treated, and pickled. Inserts, 99.5 mm x 11.8 mm x 0.5 mm, with beveled edges were laser-cut from the steel plate. The inserts were electrolytically polished to achieve a clean and smooth surface for various surface treatments. The as-received inserts were used as reference samples. Both laser-cutting and electrolytic polishing was carried out by JaloteräsStudio (West Lapland Vocational, Finland).

Silane (Dow Corning Z-6020, N-(beta aminoethyl)-gamma-aminopropyltrimethoxysilane) was used as coupling agent between plastic and metal. Without any coupling agent, polymer does not adhere to steel. Coupling agent was chosen based on our preliminary studies on different coupling agents between plastics and metals, Dow Corning Z-6020 providing the best bond strength. Commercial thermoplastic urethane - TPU - (Estane GP 85 AE nat, Lubrizol Advanced Materials, Inc., USA) was used as polymer.

2.2. Surface treatments for steel inserts

The steel inserts were surface-treated before silane treatment for better bonding between silane and steel and hence between plastic and steel. According to the literature, a metal oxide layer can improve silane-metal bonding [15,16]. In addition, the surface has to be smooth in order to achieve good bonding of silane to the metal surface [14]. The oxidation of steel 4301 was first [18] carried out by exposing it to air at 350 °C for 5-300 minutes. The oxide layer structures, characterized using transmission electron microscopy (TEM), turned out to be mainly of the types Fe_2O_3 and Cr_2O_3. The surface topographical studies of the oxide layers using atomic force microscopy (AFM) indicated that separate oxide islands were initially formed on the base oxide layer, and after 100 and 300 min exposure, the islands coalesced into an approximately 20 nm thick uniform oxide layer. According to the AFM results, smoothest surface formed after 100 min oxidation treatment [18]. Because the oxide structure and surface topography of steel 4301 was characterized in these tests [18], electrolytic polished steel inserts were oxidized in air at 350 °C for 5, 25, 100 and 300 minutes to produce a controlled surface oxide layer. In addition, earlier experiments [19] indicated that a controlled oxide layer improved the silane bonding to the steel surface. The as-received steel inserts were used as reference samples. Before silane treatment, the steel inserts were cleaned with ethanol and with acetone for 6 min in an ultrasonic cleaner (the frequency of the ultrasons was 40 kHz and the volume of the bath was 2.7 dm^3). Details of the surface treatments of the samples are described in Table 2.

2.3. Silane treatment of steel

The as-received and surface-treated steel inserts were treated before insert-injection-molding with 0.5vol.% silane at pH 9. The solution was first stirred for 1 hour, and the inserts were then dipped for 5 minutes. The inserts were cured immediately after dipping without any rinsing methods. Curing was performed in a convection oven in air at 110 °C for 10 minutes. Some of silane treatment parameters are discussed in [20].

2.4. Insert-injection-molding

TPU-steel hybrid parts were processed with an electric injection molding machine (Fanuc Roboshot aC30, Japan). The injection molding parameters are given in Table 3 and a schematic of the sample preparation of the hybrid part and the thicknesses of the components are shown in Fig. 2.

2.5. Characterization of hybrids

2.5.1. Contact angle measurements

In order to obtain detailed information about the wetting properties of different metal surfaces, the contact angles between the surface-treated stainless steel inserts and silane solution (0.5vol%) and water were measured. A goniometric contact angle measuring system (Photocomp, Finland) was used, and a constant amount of silane solution, 4 ml, or water was placed on the surface of the samples with a fixed volume pipette. The droplet was allowed to stabilize for five seconds and the contact angle values were recorded at room temperature. All measurements were repeated 10-12 times for each surface and silane solution or water and averaged.

2.5.2. Microscopic characterization

A scanning electron microscope (SEM, model XL-30, Philips, The Netherlands) was used to study the bonding of silane to the steel inserts, the plastic-metal interfaces after insert-injection-molding, and the peeled surfaces. In addition to the SEM studies, all peeled surfaces were imaged also with an optical stereomicroscope (model MZ 7.5, Leica, Switzerland). SEM, operated at an accelerating voltage of 15 kV, was equipped with an energy dispersive spectrometer (EDS, model DX-4, EDAX International, USA) and a back-scattering electron (BSE) detector. In EDS studies, silicon was used to identify the existence and distribution of silane.

2.5.3. Peel tests

The peel strength values of the finished insert-injection-molded hybrid parts were measured using 180° peel test (modification of ASTM D 903-98). Samples were conditioned before testing at 23±1 °C in 50±2% relative humidity for 72 hours. A universal testing machine (Messphysik, Austria) with a 1 kN load cell and 100 mm/min crosshead speed was used. The test was repeated 6-10 times for each insert + TPU hybrid and average values and standard deviations were calculated. A schematic drawing of the peel-test device is shown in Fig. 3.

3. RESULTS AND DISCUSSION

3.1. Contact angle measurements

Contact angle values between surface-treated stainless steel inserts and silane solution and water are shown in Fig. 4. The oxidation treatments improve the wetting properties of the steel surface. With silane solution, the contact angle values were 42 - 72 ° and with water 35 - 76 °, depending on the surface treatment of steel.

3.2. SEM studies of surface- and silane-treated steel inserts

SEM images at different magnifications of silane-treated as-received stainless steel insert are shown in Fig. 5. The silane layer is non-uniform and occurred in rings and patches on the steel surface and in some grain boundaries. The ethanol, or acetone cleaning, or electrolytic polishing of the steel insert provides similar situation than for the as-received steel as silane appears as rings and patched. However, according to the contact angle measurements, the electrolytic polished insert should show the best wetting properties. Consequently, the formation of a uniform silane layer may require a given oxide layer on the substrate [16,19].

SEM images of the silane treated + electrolytic polished + 25- and 100-min oxidized steel inserts are shown in Figs. 6 (a) and (b). On the 25-min oxidized sample, silane forms rings and waves, while on the 100-min oxidized sample, the silane layer is uniform. The silane layer was non-uniform on the electrolytic polished + 5-min oxidized sample and on the 300-min oxidized sample, the silane appears as crystallites (not shown).

SEM micrographs show that the oxide layer on a steel insert surface affects the topography of silane layer, in agreement with the findings of Susac et al. [15] and Kim et al. [16]. They found that an oxide layer improved silane bonding to an aluminum surface, and our results indicate that this is also valid for stainless steel. Previous oxidation studies [18] of stainless steel 4301, after 5- and 25-min air exposures at 350 °C, showed that separate oxide islands formed on the base oxide layer and after 100- and 300-min exposures they coalesced into a uniform oxide layer [18]. Therefore, in order to produce a uniform silane layer on a steel surface, a uniform oxide layer is required on the steel before silane treatment. Good bonding of silane requires a smooth substrate because a rough surface can prevent silane layer formation on the surface [14]. Based on our earlier studies, the smoothest surface of the steel is formed after 100 min oxidation treatment [18].

Injection molding was carried out with the acetone-cleaned as-received, electrolytic polished, electrolytic polished + 5-min oxidized, electrolytic polished + 100-min oxidized, and electrolytic polished + 300-min oxidized steel inserts. Before molding, each steel insert was treated with silane.

3.3. SEM studies of insert-injection-molded hybrid parts

The silane layers and interfaces, TPU/silane and silane/insert, of the hybrid parts were studied in the perpendicular direction to the melt flow by SEM. SEM images of cross-sections of injection-molded hybrids produced with as-received and with electrolytic polished + 5-min oxidized steel insert are shown in Figs. 7 (a) and (b). On both the as-received and electrolytic polished + 5-min oxidized steel inserts, the silane layers are non-uniform, but silane islands are larger in the electrolytic polished + 5-min oxidized insert. By increasing the oxidation time to 100 min, a uniform silane layer 2-6 μm thick (Fig. 8) appears and at high magnification (Fig. 8) it is shown that silane bonds well to steel. The oxide layer under the silane layer is too thin to be detected by SEM. The cross-sectional SEM image and the corresponding Si-mapping of the injection-molded hybrid with the electrolytic polished + 100-min oxidized steel insert are shown in Fig. 9, indicating that the uniform silane layer is also shown by using Si-mapping. On the electrolytic polished + 300-min oxidized steel insert, the silane layer was close to uniform but varied significantly in thickness, up to more than 5 μm.

3.4. Bond strengths of insert-injection-molded hybrid parts

Bond strengths of the insert-injection-molded hybrid parts were determined from 180° peel tests (Fig. 10). The combined electrolytic polishing and oxidation of the steel inserts improves the bond strength of the hybrids. The highest bond strength is achieved with electrolytic polished + 5-min oxidized steel insert. The uniform silane layer on the electrolytic polished + 100-min oxidized steel insert is probably too thick to achieve the highest bond strength [9].

3.4.1. Stereomicroscopic characterization of peeled surfaces

Peeled surfaces, steel and TPU sides, were studied with optical stereomicroscope to characterize their loci of failure. Stereomicroscope images of the failed surfaces on the hybrid with an as-received steel insert and with an electrolytic polished + 5-min oxidized steel insert after peel test are shown in Figs. 11 (a) and (b), respectively. A few TPU islands appear on the peeled as-received steel insert surface which indicates more than 95% adhesive failure in the as-received steel insert + TPU hybrid. While, the peeled electrolytic polished + 5-min oxidized steel insert surface is almost covered with TPU which indicates that a cohesive failure in TPU had occurred. The loci of failure in all electrolytic + polished + oxidized steel inserts are cohesive to a larger extent in TPU than for the as-received steel insert.

3.4.2. SEM characterization of peeled surfaces

As-received steel + TPU hybrid

The peeled surfaces were studied by SEM to gain more information about the loci of failure of the hybrids. The failed steel surface of the as-received steel insert + TPU hybrid after peel test is shown in Figs. 12 (a) and (b). A cohesive failure in the TPU and adhesive failure or cohesive failure in the silane layer is obtained. TPU residues remaining on the failed steel surface after peel test are seen in Fig. 12 (a) and some grain boundaries containing silane are visible in Fig. 12 (b). The failed TPU surface of the as-received steel insert + TPU hybrid after peel test is shown in Figs. 12 (c) and (d). In the TPU failed surface (Fig. 12 (d)), the grain boundaries of the steel insert are visible. According to EDS analysis (not shown), Si is detected in the “replica grain boundaries” on the peeled TPU surface. Consequently, silane remained on both steel and TPU sides, indicating the occurrence of mixed failure mode.

Electrolytically polished and 5 min oxidized steel + TPU hybrid

Failed surfaces, steel and TPU sides, of the electrolytically polished and 5-min oxidized steel insert + TPU hybrid after peel test are shown in Figs. 13 (a) and (b). Mainly a cohesive failure in the TPU appears but also some areas with silane remaining on the TPU side are present. Silane remains also on the failed steel surface. The loci of failure are therefore similar to those of the as-received steel insert + TPU hybrid; however, the cohesive failure in the TPU dominates the electrolytic polished + 5-min oxidized steel insert + TPU hybrid. Failed surfaces of the electrolytic polished + 100-min oxidized steel insert + TPU hybrid are very similar to those of the electrolytic polished and 5-min oxidized steel insert + TPU hybrid and a cohesive failure in the TPU dominates.

Cross-sectional analysis of peeled steel surface

The loci of failure of the TPU-metal joints were also studied by analyzing the cross-sections of the peeled steel surface. Different regions at the interface on the peeled steel surface were ascribed to TPU/silane, and steel/silane, and to cohesive failure within the TPU and/or the silane. The TPU/silane and steel/silane failure interfaces show an adhesive failure. On the other hand, the cohesive failure in TPU or in silane indicates excellent bonds between silane and steel and between silane and TPU. Three different regions at the interface of the failed electrolytic polished + 100-min oxidized steel insert after peel test are shown in Figs. 14 (a) - (c). A bare steel surface with the failure occurring at the silane/steel interface which indicates weak silane bonding to the steel is shown in Fig 14 (a). Silane remains on the steel in Fig. 14 (b), and failure occurs at the TPU/silane interface or within the silane layer. A cohesive failure occurs in TPU in Fig. 14 (c) with silane and TPU remaining on the steel surface. A cohesive failure in the TPU dominates in the peeled electrolytic polished + 100-min oxidized steel insert + TPU hybrid.

4. CONCLUSIONS

This study aimed to investigate the adhesion between thermoplastic urethane (TPU) and stainless steel in insert-injection-molded hybrid parts using silane coupling agent. Before silane treatment, steel insert surfaces were differently treated to achieve a better bonding between silane and steel and hence between TPU and steel.

Contact angle measurements, microscopic studies, and adhesion tests showed that electrolytic polishing and oxidation of steel inserts improved silane bonding to steel and, consequently, TPU adhesion to steel. An adhesive failure occurs in steel + TPU hybrids at the different interfaces, i.e. silane/steel and TPU/silane. With electrolytic polished and oxidized steel inserts, the locus of failure was more cohesive in the TPU than with as-received steel insert because of better silane bonding to the surface-treated steel. Further studies are required to more carefully analyse the interfaces and the long-term stability of hybrids produced with variously surface-treated inserts to gain information about the effects of the uniformity/non-uniformity of the silane layer. Silane treatment parameters must also be optimized to achieve the most optimum uniform silane layer.

Acknowledgements

Financial support by Graduate School of Processing of Polymers and Polymer-based Multimaterials (POPROK) and by Finnish Funding Agency for Technology and Innovation (TEKES) is acknowledged.

References:

[1] G. Zhao and G. Ehrenstein, In: *Proceedings of SPE Annual Technical Conference (ANTEC 1999)*, New York, USA, pp. 1332-1336 (1999).

[2] O. Zoellner and J. Evans, In: *Proceedings of SPE Annual Technical Conference (ANTEC 2002)*, San Francisco, CA, USA, pp. 1-4 (2002).

[3] B. Pugh, *Reinforced Plastics* **4**, 27 (1997).

[4] T. Palmer, *Machine Design* **76**, 76-80 (2004).

[5] M. Grujicic, V. Sellappan, M. Omar, N. Seyr, A. Obieglo, M. Erdmann and J. Holzleitner, *J. Mater. Process. Technol.* **197**, 363-373 (2008).

[6] P. Fabrin, M. Hoikkanen and J. Vuorinen, In: *Proceedings of SPE Annual Technical Conference (ANTEC 2007)*, Cincinnati, OH, USA, pp. 2528-2532 (2007).

[7] G. Pritchard (Ed), *Plastic Additives.* p. 683. Chapman & Hall, London (1998).

[8] A guide to silane solutions, http://www.dowcorning.com (21.9.2007).

[9] E. Plueddemann, *Silane Coupling Agents*, p. 235. Plenum Press, New York (1982).

[10] V. Subramanian and W.J. van Ooij, *Corrosion* **54**, 204-215 (1998).

[11] K. Weissenbach and H. Mack, in: *Functional Fillers for Plastics*, M. Xanthos (Ed.), pp. 59-83, Wiley-VCH, Weinheim (2005).

[12] J. Flis and M. Kanoza, *Electrochim. Acta* **51**, 2338-2345 (2006).

[13] M.-L. Abel, R. Allington, R. Digby, N. Porritt, S. Shaw and J. Watts, *Int. J. Adhesion Adhesives* **26**, 2-15 (2006).

[14] E.M. Petrie, *Handbook of Adhesives and Sealants*. p. 902. McGraw-Hill, New York (2000).

[15] D. Susac, X. Sun and K. Mitchell, *Appl. Surf. Sci.* **207**, 40-50 (2003).

[16] J. Kim, P. Wong, K. Wong, R. Sodhi and K. Mitchell, *Appl. Surf. Sci.* **253**, 3133-3143 (2007).

[17] F. Boerio and P. Shah, *J. Adhesion* **81**, 645-675 (2005).

[18] M. Honkanen, M. Vippola and T. Lepistö, *Surface Engineering*, in press.

[19] M. Honkanen, M. Vippola, K. Rissa, T. Lepistö, M. Hoikkanen and J. Vuorinen, In: *Proceedings of the 58th Annual Meeting of the Scandinavian Society for Electron Microscopy*, Helsinki, Finland, pp. 75-76 (2007).

[20] M. Hoikkanen, M. Honkanen, A. Luukkonen, M. Vippola, J. Vuorinen and T. Lepistö, In: *Proceedings of International Rubber Conference*, Kuala Lumpur, Malaysia, p. 11 (2008).

Table captions:

Table 1. Nomenclature and chemical composition of steel material used.

Table 2. Summary of different surface treatments for steel inserts.

Table 3. Injection molding parameters.

Figure captions:

Figure 1. Hydrolysis and condensation of alkoxysilane and its bonding to inorganic surface, modified from [8].

Figure 2. Schematic of preparation of hybrid part and thicknesses of different hybrid part components.

Figure 3. Schematic drawing of peel-test device.

Figure 4. Average contact angle values and standard deviations of silane solution and water on pre-treated stainless steel inserts.

Figure 5. SEM images of silane-treated, as-received stainless steel insert.

Figure 6. SEM images of silane treated + electrolytic polished + (a) 25 min oxidized and (b) 100 min oxidized steel inserts.

Figure 7. Cross-sectional SEM images of insert-injection-molded hybrids made with (a) acetone cleaned, as-received steel insert, and (b) electrolytic polished + 5 min oxidized steel insert.

Figure 8. Cross-sectional SEM images of insert-injection-molded hybrid made with electrolytic polished + 100 min oxidized steel insert.

Figure 9. Cross-sectional SEM image and Si-map of insert-injection-molded hybrid made with electrolytic polished + 100 min oxidized steel insert.

Figure 10. Peel strength values and standard deviations of insert-injection-molded hybrid parts made with differently treated steel inserts.

Figure 11. Stereomicroscope images of failed surfaces (TPU and steel) after peel test. (a) Acetone-cleaned, as-received steel insert + TPU and (b) electrolytic polished + 5 min oxidized steel insert + TPU.

Figure 12. Failed surfaces of acetone-cleaned as-received steel insert + TPU hybrid after peel test. SEM images of (a) TPU islands on steel side, (b) steel surface, (c) and (d) TPU side.

Figure 13. Failed surfaces of electrolytic polished and 5 min oxidized steel insert + TPU hybrid after peel test. (a) Steel side, (b) TPU side.

Figure 14. Different interfaces in electrolytic polished + 100 min oxidized steel insert after peel test. (a) Bare steel surface, (b) silane remaining on steel surface, and (c) silane and TPU remaining on steel surface.

Table 1. Nomenclature and chemical composition of steel material used.

Nomenclature		Chemical composition [wt%]						
EN	ASTM	C	Cr	Ni	Si	Mn	P	S
1.4301	AISI 304	0.05	18.2	8.2	0.53	1.7	0.03	0.001

Table 2. Summary of different surface treatments for steel inserts.

As-received (reference, no surface treatment)
Ethanol cleaning
Acetone cleaning in ultrasonic bath
Electrolytic polishing
Electrolytic polishing + oxidation 350°C/5min
Electrolytic polishing + oxidation 350°C/25min
Electrolytic polishing + oxidation 350°C/100min
Electrolytic polishing + oxidation 350°C/300min

Table 3. Injection molding parameters.

Speed (injection)	20 mm/s
Temperature (mold)	50°C
Back pressure	750 bar (for 3 s)
Cooling time	15 s
Plastization flow rate and back pressure	50 rpm, 10 bar
Temperature (cylinder)	200 - 195 - 190 - 185 - 35°C

Figure 1.

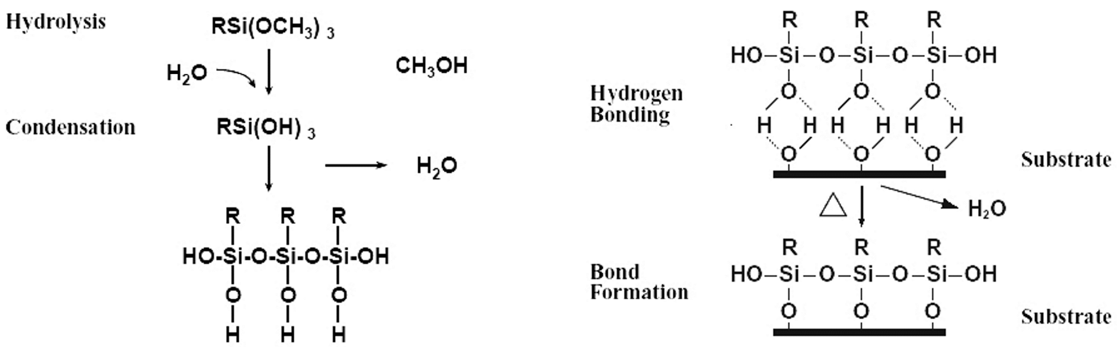


Figure 2.

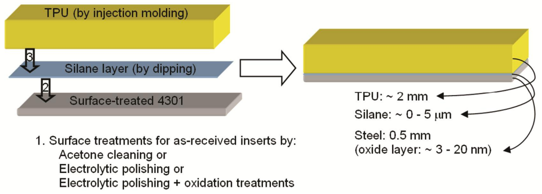


Figure 3.

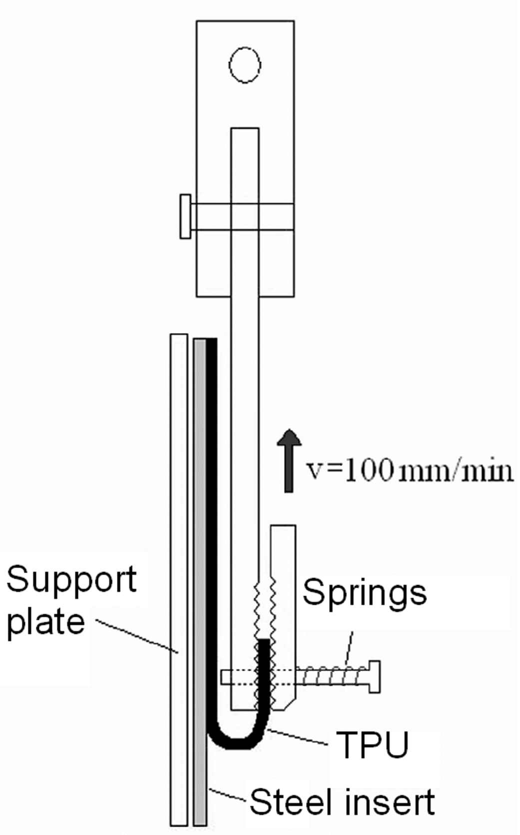


Figure 4.

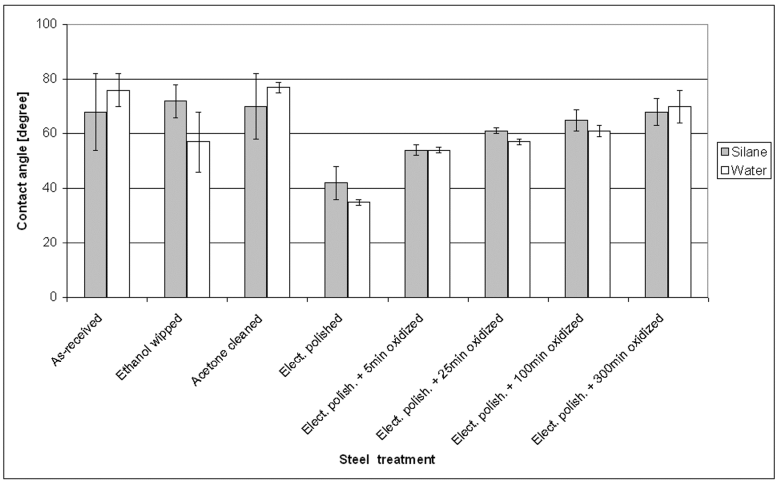


Figure 5.

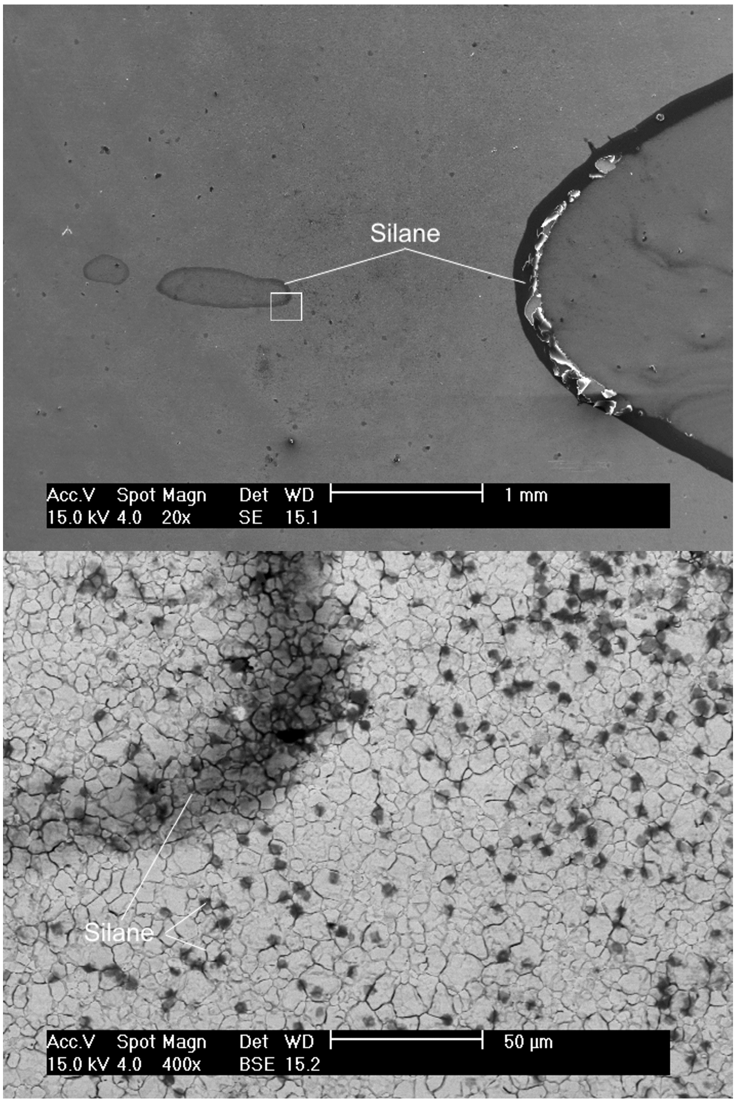
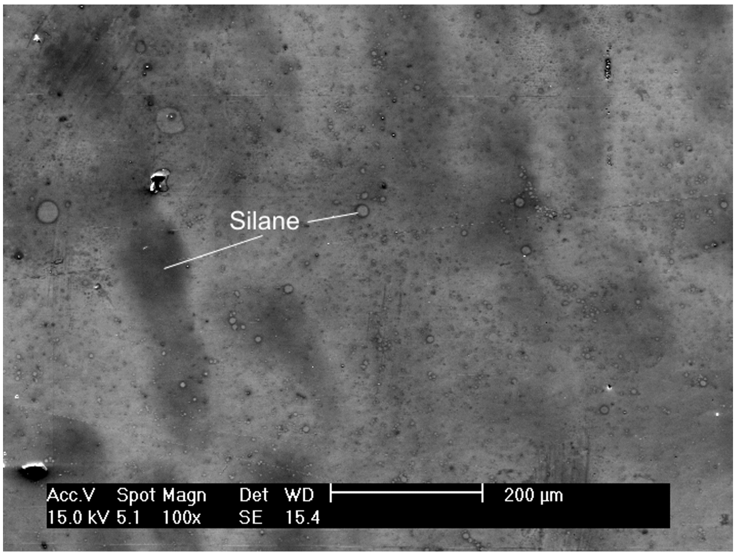
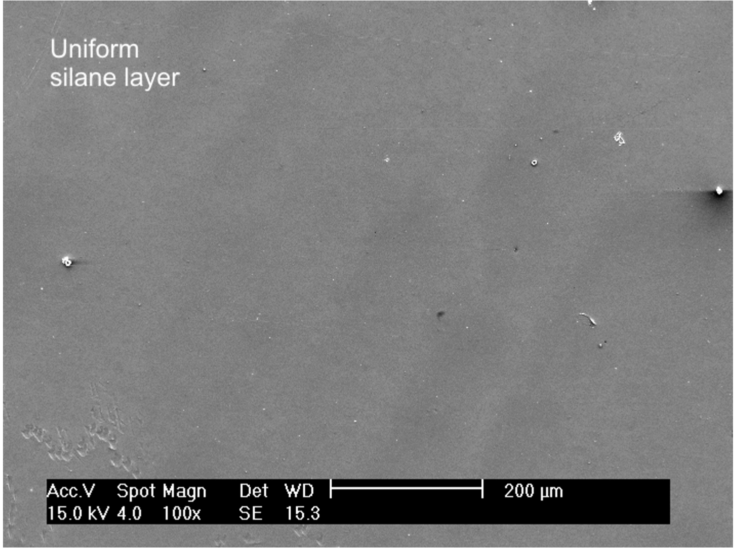


Figure 6.

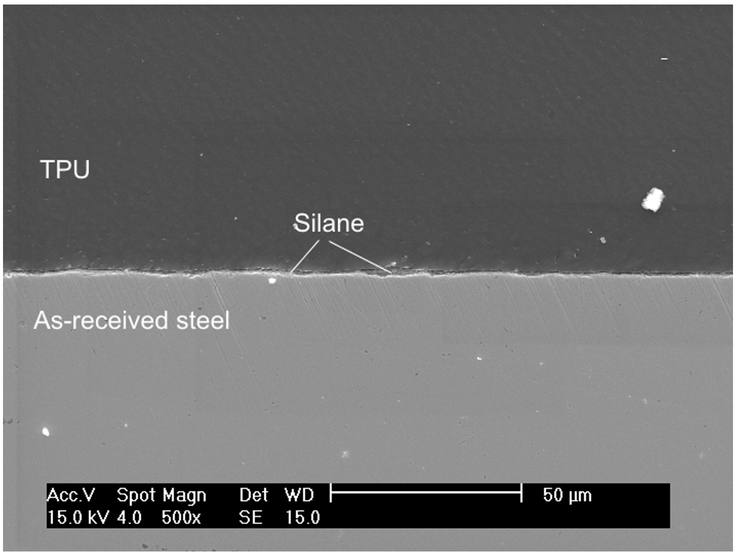

Silane
Acc.V Spot Magn Det WD 200 µm
15.0 kV 5.1 100x SE 15.4

(a)


Uniform
silane layer
Acc.V Spot Magn Det WD 200 µm
15.0 kV 4.0 100x SE 15.3

(b)

Figure 7.


TPU
Silane
As-received steel
Acc.V Spot Magn Det WD 50 µm
15.0 kV 4.0 500x SE 15.0

(a)

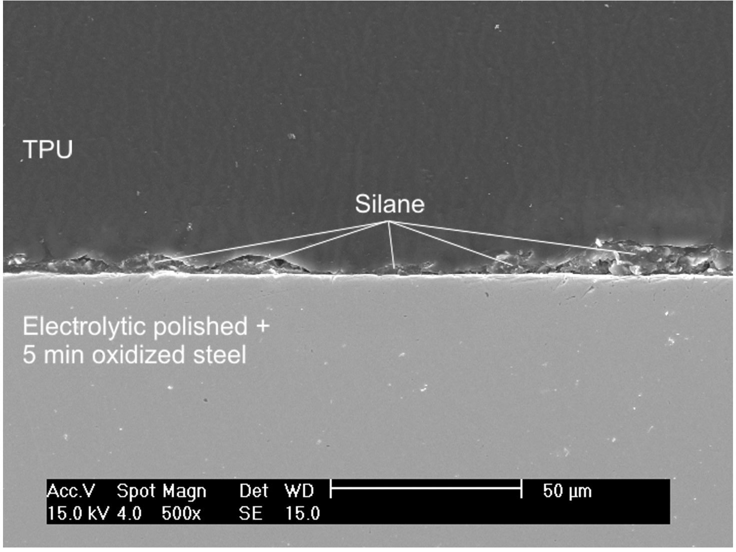

TPU
Silane
Electrolytic polished +
5 min oxidized steel
Acc.V Spot Magn Det WD 50 µm
15.0 kV 4.0 500x SE 15.0

Figure 8.

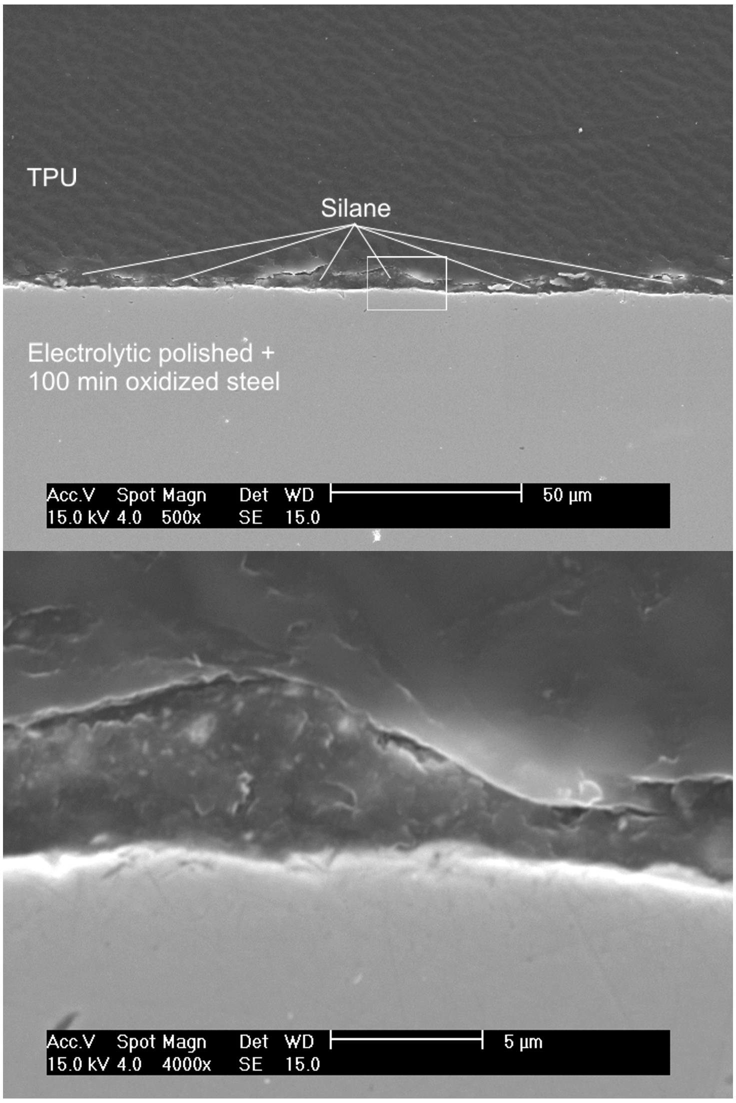

TPU
Silane
Electrolytic polished +
100 min oxidized steel
Acc.V Spot Magn Det WD 50 µm
15.0 kV 4.0 500x SE 15.0
Acc.V Spot Magn Det WD 5 µm
15.0 kV 4.0 4000x SE 15.0

Figure 9.

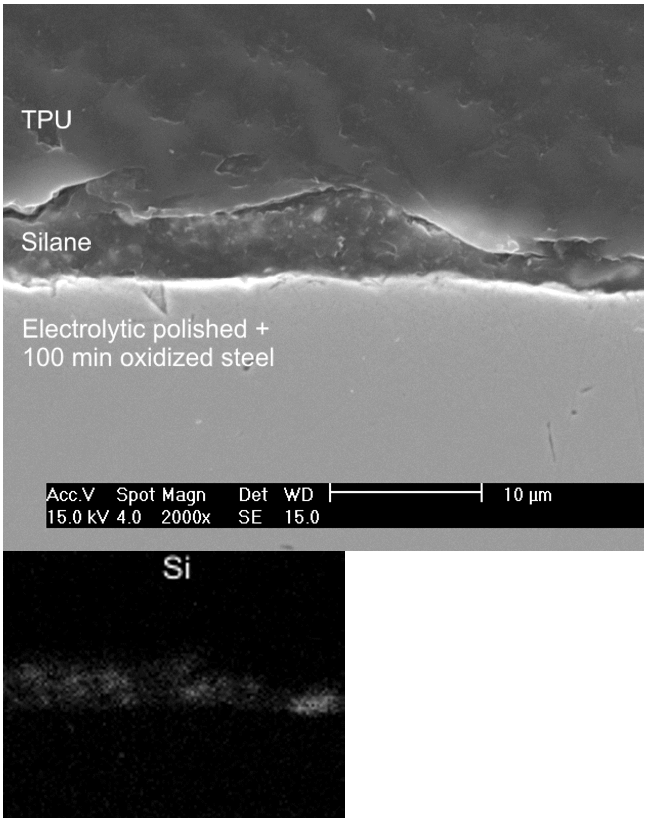


Figure 10.

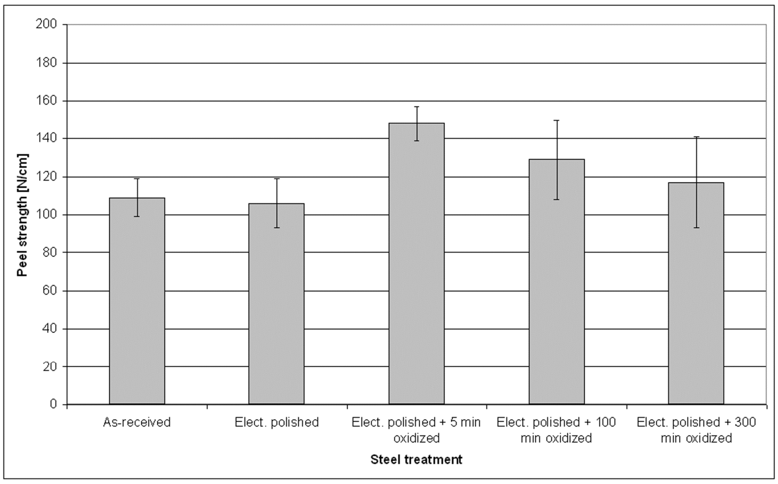


Figure 11.

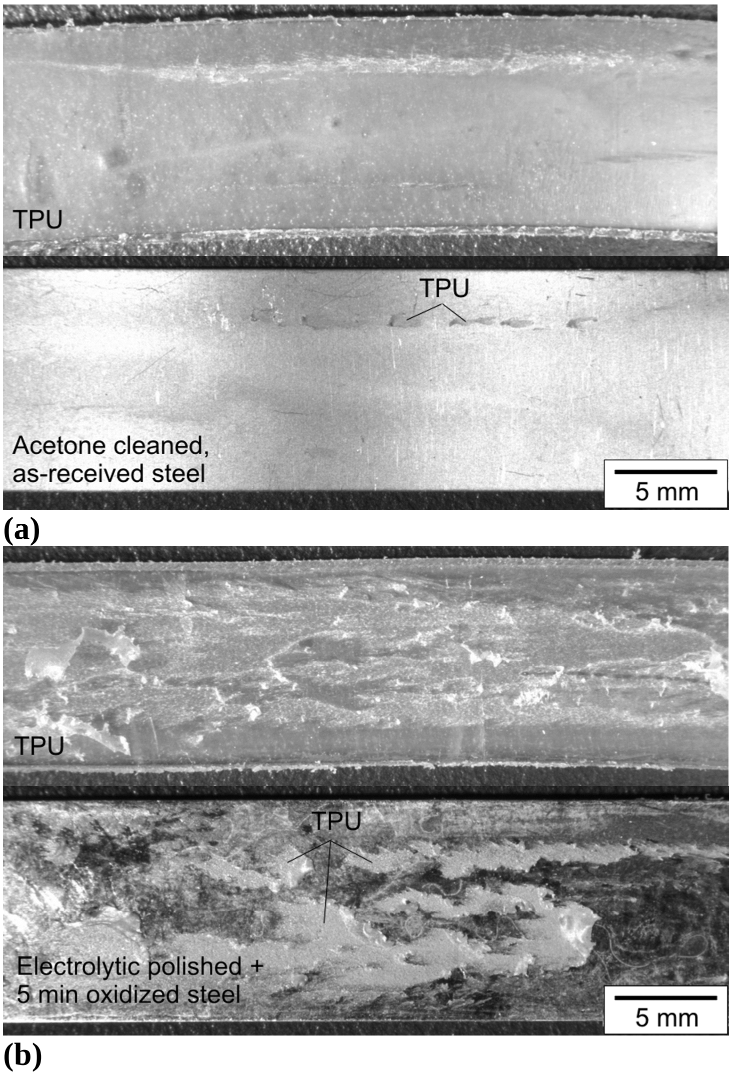
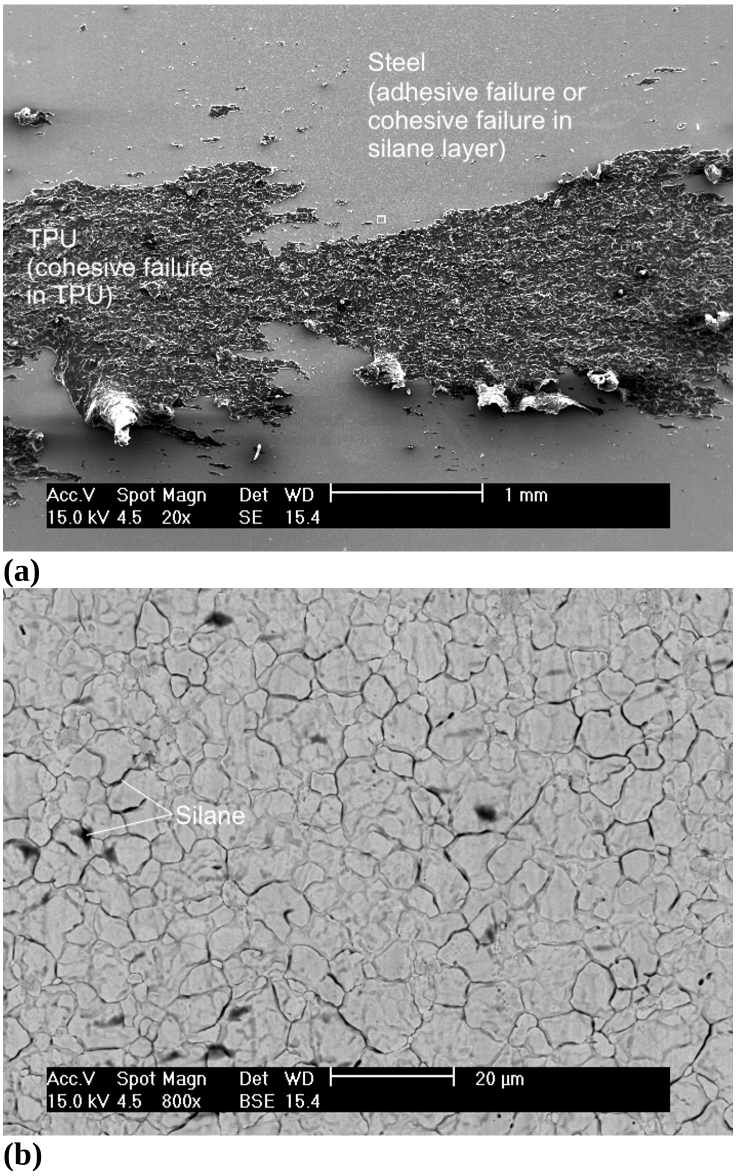
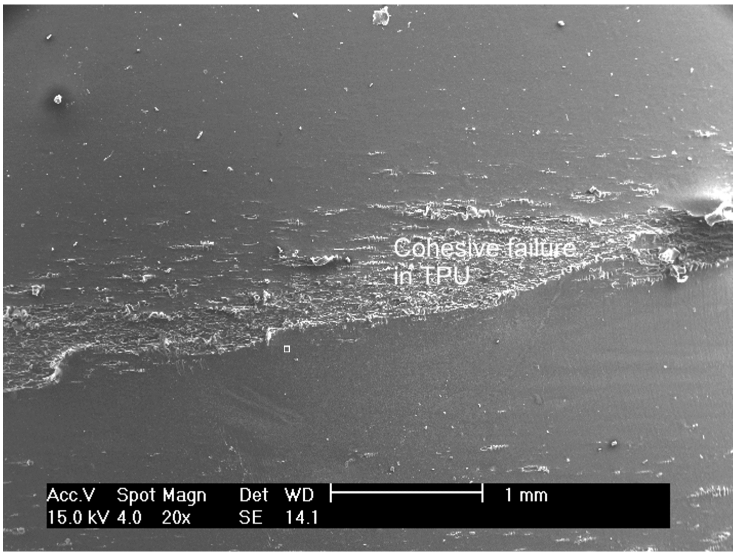
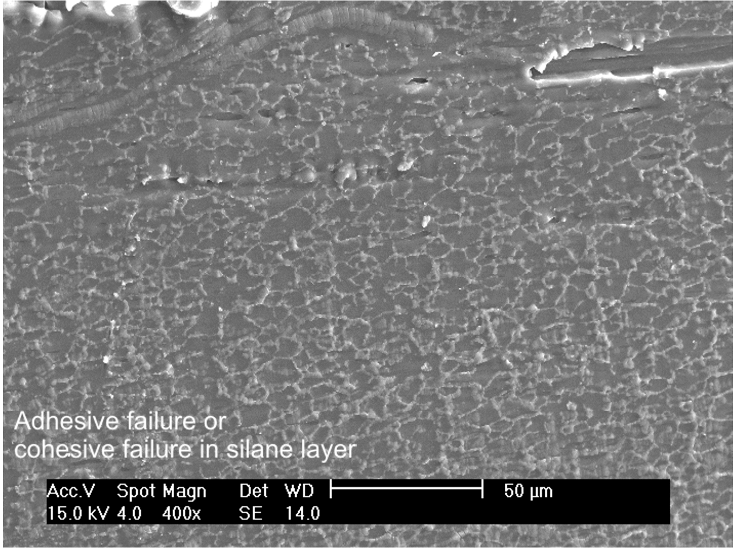

TPU
TPU
Acetone cleaned,
as-received steel
5 mm
(a)
TPU
TPU
Electrolytic polished +
5 min oxidized steel
5 mm
(b)

Figure 12.


Steel
(adhesive failure or
cohesive failure in
silane layer)
TPU
(cohesive failure
in TPU)
Acc.V Spot Magn Det WD 1 mm
15.0 kV 4.5 20x SE 15.4
(a)
Silane
Acc.V Spot Magn Det WD 20 µm
15.0 kV 4.5 800x BSE 15.4
(b)

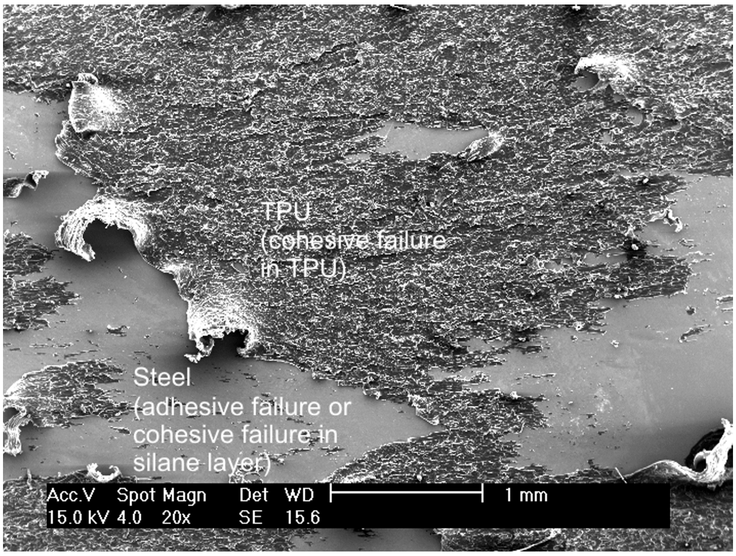

Cohesive failure in TPU
Acc.V Spot Magn Det WD 1 mm
15.0 kV 4.0 20x SE 14.1

(c)

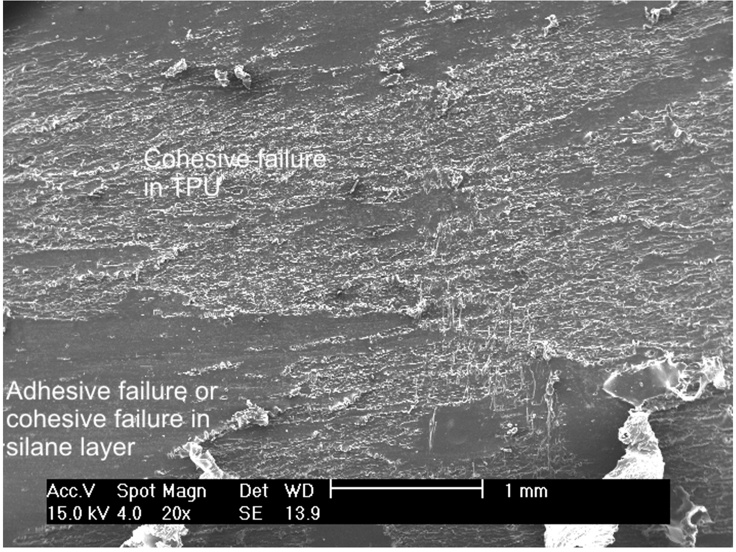

Adhesive failure or cohesive failure in silane layer
Acc.V Spot Magn Det WD 50 µm
15.0 kV 4.0 400x SE 14.0

(d)

Figure 13.

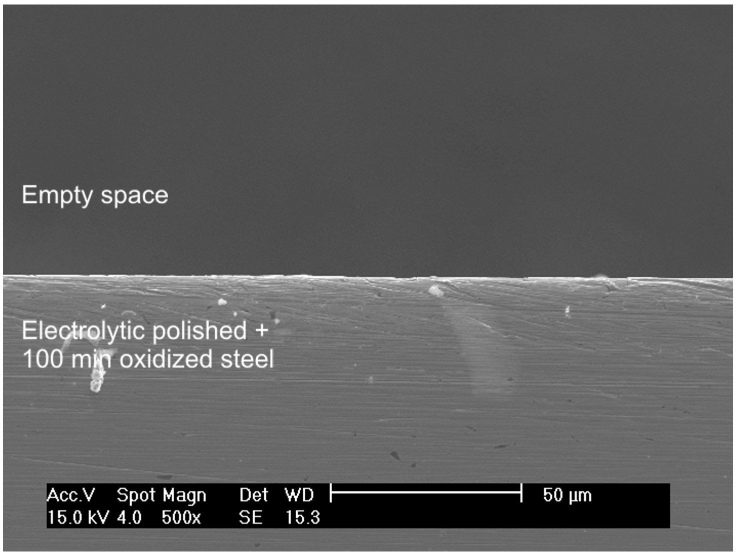

TPU
(cohesive failure
in TPU)
Steel
(adhesive failure or
cohesive failure in
silane layer)
Acc.V Spot Magn Det WD 1 mm
15.0 kV 4.0 20x SE 15.6

(a)

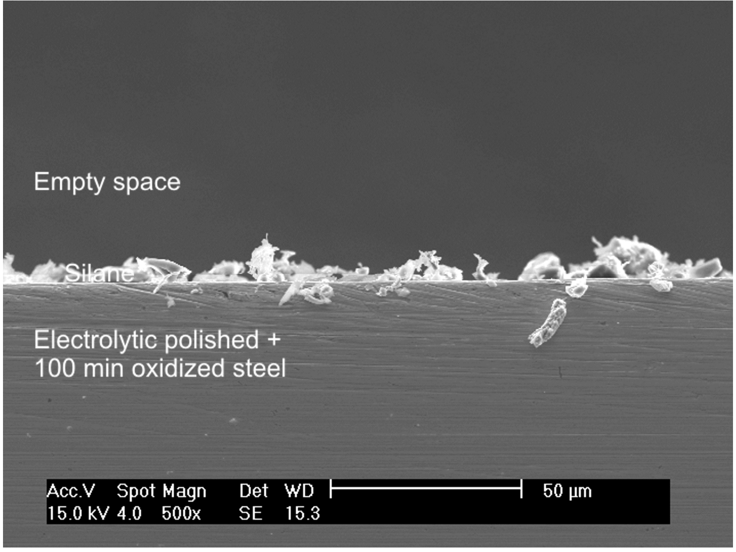

Cohesive failure
in TPU
Adhesive failure or
cohesive failure in
silane layer
Acc.V Spot Magn Det WD 1 mm
15.0 kV 4.0 20x SE 13.9

(b)

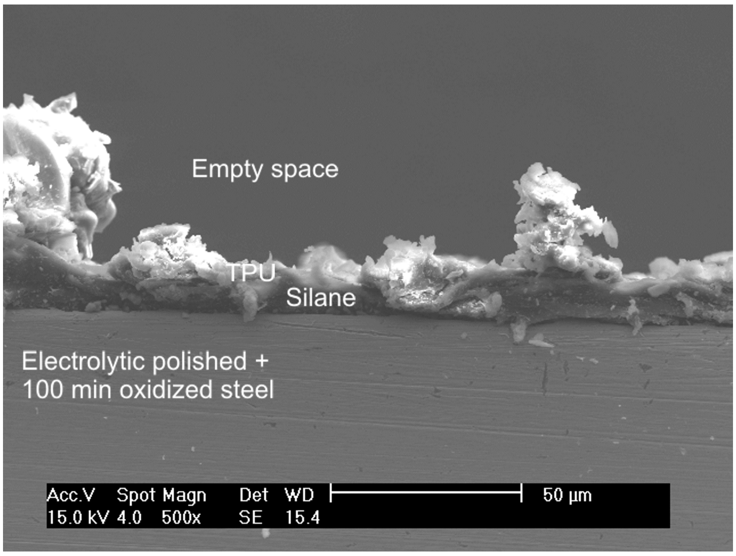
Figure 14.


Empty space
Electrolytic polished +
100 min oxidized steel
Acc.V Spot Magn Det WD
15.0 kV 4.0 500x SE 15.3
50 µm

(a)


Empty space
Silane
Electrolytic polished +
100 min oxidized steel
Acc.V Spot Magn Det WD
15.0 kV 4.0 500x SE 15.3
50 µm

(b)


Empty space
TPU
Silane
Electrolytic polished +
100 min oxidized steel
Acc.V Spot Magn Det WD
15.0 kV 4.0 500x SE 15.4
50 µm

(c)