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## ASSESSMENT OF ALTERNATIVE SURFACE MODIFICATION TECHNOLOGIES FOR IMPROVED ADHESION OF COATINGS AND ADHESIVES TO AUTOMOTIVE POLYOLEFINS

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**Key words:** automotive plastics, polyolefins, surface modification, bonding, adhesives, surface coatings, sealants, adhesion strength, durability.

**Abstract:** Thermoplastic olefins (TPO's) are important materials for the manufacture of exterior and interior automotive components due to their low cost, reduced specific density in comparison with other types of plastics, easy processing, and 100% recyclability. Nano-composites with TPO matrix additionally offer significant gains in strength and impact resistance due to excellent interfacial reinforcement effect, a high modulus of elasticity, and the matrix ductility. Typical automotive products made of standard TPO's and PP-based nanocomposites include: bumper bars, protective bodyside mouldings, exterior and interior cladding, e.g., door trim panels, instrument panels, gearbox console and seat structure components. One of key drawbacks of TPO's is their chemical inertness. This necessitates priming or appropriate surface treatment to enable the assembly of products through adhesive bonding and to facilitate adequate adhesion of paints, sealants, or other functional and decorative materials. Considering the above, the objective of this paper is two-fold: (1) To investigate and assess a range of processes for enhancing adhesion of TPO's, e.g., flame treatment, chlorinated polyolefin (CPO) primers and a proprietary surface engineering process (SICORä) of TPO's and other plastics and assess their suitability for a range of applications in automotive products, and (2) To demonstrate practical examples of the use of SICORä process for adhesion control in the automotive industry.

### Ocena alternatywnych technologii modyfikacji powierzchni dla ulepszonej adhezji powłok i klejów na poliolefinach samochodowych

**Słowa kluczowe:** tworzywa sztuczne samochodowe, poliolefiny, modyfikacja powierzchni, klejenie, kleje, powłoki powierzchniowe, uszczelniacze, wytrzymałość adhezyjna, trwałość.

**Streszczenie:** Termoplastyczne olefiny (TPO) są ważnymi materiałami do produkcji zewnętrznych i wewnętrznych części samochodowych ze względu na ich niski koszt, zmniejszoną gęstość właściwą w porównaniu z innymi rodzajami tworzyw sztucznych, łatwą obróbkę i niemal 100% możliwość recyklingu. Nanokompozyty z matrycą TPO dodatkowo oferują znaczny wzrost wytrzymałości i odporności na uderzenia dzięki doskonałemu oddziaływaniu wzmacniającemu międzyfazowy efekt, wysokiemu modułowi sprężystości i plastyczności matrycy. Typowe produkty motoryzacyjne wykonane ze standardowych nanokompozytów na bazie TPO i PP obejmują: zderzaki, listwy ochronne, zewnętrzne panele karoserii i panele wewnętrzne, np. panele drzwi, deski rozdzielcze, konsole skrzyni biegów i elementy konstrukcji siedzenia. Jedną z głównych wad TPO jest ich obojętność chemiczna. Wymaga to gruntowania lub odpowiedniej obróbki powierzchni, aby umożliwić montaż produktów poprzez klejenie i ułatwić odpowiednią przyczepność (adhezję) farb, uszczelniaczy lub innych materiałów funkcjonalnych i dekoracyjnych. Biorąc powyższe pod uwagę, cel niniejszego artykułu jest dwójaki: (1) Zbadanie i ocena szeregu procesów zwiększających przyczepność (adhezję) TPO i innych tworzyw sztucznych, np. obróbka płomieniowa, podkłady chloro-poliolefinowe (CPO) i zastrzeżony proces inżynierii powierzchni (SICORä) oraz ocena ich przydatności do wielu zastosowań w produktach motoryzacyjnych, oraz (2) przedstawienie praktycznych przykładów wykorzystania procesu SICORä do kontroli przyczepności (adhezji) w przemyśle motoryzacyjnym.

## 1. Polymer Surface Treatments

### 1.1. Current technologies

Various surface pre-treatments, including chemical, flame, corona discharge, and plasma treatments are known to improve the bonding ability of polymers. Most of these processes are oxidative in nature. The incorporation of oxygenated chemical species onto the surface of polymers by flame, air corona, or other oxidative treatments is generally sufficient to provide a surface receptive enough for some types of adhesives or paints. However, it is frequently essential to tailor the surface properties in order to enhance preferable interactions across the substrate-adhesive or substrate-paint interface. Plasma treatment can be used for this purpose. The process allows for the incorporation of a wide range of surface chemical species onto polymer surface. One of the major disadvantages of plasma treatment, especially in the case of low value-added products, is its relatively high cost due to the need for vacuum equipment, typically necessitating batch processing. Although continuous plasma equipment has been described in literature, its technological applications are limited to high value-added products.

Currently, the most effective method for enhancing the adhesion of paints to automotive TPO's is priming with solvent-based chlorinated polyolefin primer (CPO's). These are spray-applied onto the surface of power-washed or flame treated TPO-based products. Their disadvantage is the high content of VOCs, cost lack of effective for enhancing adhesion of adhesives.

### 1.2. SICORä Process

The SICORä process [1–9], owing its name to the original processing sequence: i.e. 'SIlane on CORona-oxidised polymer surface, enables simple incorporation of optional surface functional groups onto the surface of polymeric substrates. This facilitates the tailoring of surface chemistry with the aim of controlling adhesion between surface-engineered substrates and adjacent materials, e.g., adhesives, paints, printing inks, sealants, or other materials.

The process, schematically depicted in Fig. 1, comprises the following: (1) surface oxidation by a physical and/or physico-chemical means, e.g., flame, corona discharge, UV treatment or wet-chemistry means providing appropriate receptive sites, e.g., OH, C = O, COOH, reactive with functional groups of connector molecules, followed by (2) application of poly-functional chemicals capable of forming hydrogen, or covalent bonds with these surface groups, e.g., organo-functional silanes, organometallic compounds (e.g., organo-zirconates, -titanates, -tin compounds, -aluminates, etc.) or alternatively, long-chain bi-functional or poly-functional macromolecules such as poly-functional amino-compounds – linear or branched. The functionality of pendant groups, as illustrated in Figure 1(b), is chosen to provide surface chemical reactivity with adhesives, paints, metallic coatings, or other materials to be brought into contact with the surface-modified polymer.

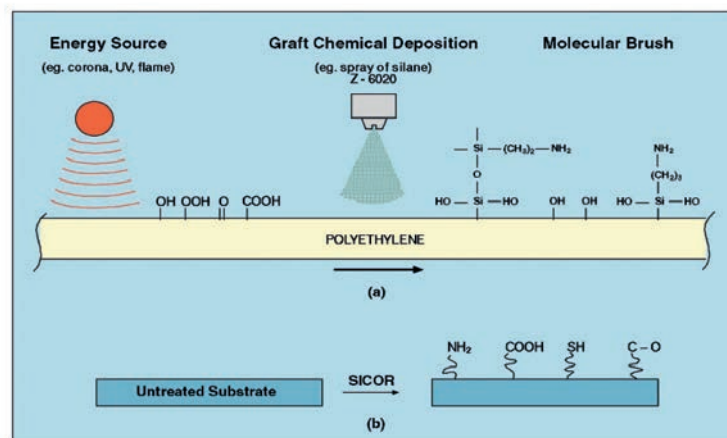


Fig. 1. Schematics of “SICOR” process: (a) process flow in a continuous mode, and (b) substrate surface transformation from ‘bare’ to ‘decorated’ with molecular brush arrays

The above process facilitates: (i) continuous and inexpensive incorporation of a wide range of surface functional groups onto the surface of a polymeric products with relatively minor adaptation of existing factory plant and equipment, and (ii) the possibility of

tailoring the surface chemistry of a polymeric product without altering its bulk properties, so that the adhesion between the surface engineered substrate and adhesive, paint, printing ink, or other materials is optimised.

## 2. Experimental

### 2.1. Methods

**Substrate oxidation:** Surface oxidation was carried out by flame or corona discharge treatment. The latter was conducted using a Tantec EST, HV 2010 unit (adjustable power output up to 1 kW). The distance between the substrate surface and electrode was maintained at 2.5 mm in this work. Treatment speed range was controlled between 0.1 to 70 m/min.

Flame treatment was carried out using an Arcotec EFT 751 system equipped with a 200 mm burner providing 50 kW energy output at 1.0% excess oxygen in the air/propane mixture. The treatment distance (between the flame tip and substrate surface) is adjustable within 5–130 mm. In this work, it was kept at 10 mm for flat substrate samples, whilst for 3-D products (instrument panels, door trim panels, etc.), the robot was programmed to ensure the flame tip distance within 10–50 mm range. Treatment speed was controlled in the range of 20–90 m/min.

**Chlorinated Primer (CPO) priming:** A chlorinated primer (CPO) with 6% solids content commonly used in automotive paint shops worldwide was used for benchmarking in order to assess the quality and industrial applicability of SICOR process versus current technologies. It was sprayed at a recommended rate (approx. 3  $\mu\text{m}$  coating thickness) onto the surface of either the power-washed or flame-treated TPO substrates.

**Preparation and application of graft chemicals:** Graft chemicals were diluted with deionized water to obtain the required concentration. The standard concentration of chemical solutions throughout most experiments, industrial trials, and subsequent production was 0.1, 0.25, or 0.5%, depending on the type of application.

### 2.2. SICOR Process Configuration

#### *Pilot Plant and Industrial Units*

The substrate samples, or full-size automotive components (e.g., BSPM) are treated using an on-line SICOR unit in three consecutive steps: (1) Flame oxidation: 20–90 m/min; (2) Graft chemical spray, followed by (3) Infra-Red (IR) or hot air flash-off at 80°C.

#### *Laboratory Procedures*

The substrates, treated by flame or corona discharge, were immersed in the graft chemical solution for 30 s, after which the samples were dried in air for 30 min, followed by oven drying at 40°C. After initial experiments, the oven-drying was abandoned since no significant difference was observed between the air- and oven-dried specimens. The dip in a chemical solution

was replaced by an on-line spray application carried out immediately after corona discharge or flame treatment, followed by a flash-off implemented by an infrared drying element or hot air.

### 2.3. Materials

#### *Substrates*

The following polymers were used in experiments:

**Laboratory scale: Homopolymers:** Low density polyethylene (LDPE); polypropylene (PP); ultra-high molecular weight polyethylene (UHMW-PE); **Automotive TPO blends:** the BSPM grade blend used throughout the process development and industrial tests was a talc-filled PP designated as Corton 1054/2 HS: in the following grades: (i) Natural (no pigment), (ii) Black, and (iii) Grey. A bumper grade PP/EPDM blend was also used. All materials, based on Montell polymers, were supplied by PolyPacific/Australia.

**Production trials (type of automotive component and TPO material used):**

- (i) Instrument panels: Extron PDR 3039 HS7386 (Polypacific/Melbourne),
- (ii) Door trim panels: Jazz 012/4 (recycled TPO – Polypacific/Melbourne),
- (iii) Bodyside protective mouldings: PD0046.40 (210910) (CompCo/Melbourne).

#### *Paints*

The test plaques and production components were SICOR treated and painted with basecoat/clear coat supplied by PPG using the following coatings: **Basecoats:** *Heron White; Quick Silver; Tungsten; Hyper; Redhot; Shanghai; Botticelli; Laurel; Delft; Vespers; Phantom; Dark Chestnut; Hot House Green; Yellow Devil.* **Clearcoat:** 2-part polyurethane.

#### *Adhesives and Sealants*

**Adhesives:** (1) structural acrylic: *Permabond F-241, Permabond*; (2) cyanoacrylate: *Loctite 406, Loctite Corp*; (3) structural epoxy: *Araldite 138 M-1 (Huntsman)*; structural polyurethane: (4) 7520 A/B (Lord Corp); (5) flexible polyurethane (PU): *Bostik 8104*

**Elastomeric sealants:** polyurethane (PU): *Betaseal 55402 (Expandite-Essex)*,

**Self-adhesive tapes:** (1) VHB 4959, 3 mm thick, (2) 4220, 0.42 mm thick (both from 3M).

**Graft chemical types:** (1) *Silanes:* N-(2-aminoethyl)-3-aminopropyltrimethoxysilane: Z-6020 and 3-glycidoxypropyltrimethoxysilane: Z-6040 (both from Dow Corning), and (2) *Polyethylene imines (PEI):* MW (weight average) 800; 2000; 25,000; 750,000 (all, BASF).

### Coverstock material

PVC skin/polyethylene foam was used for vacuum-wrapping (lamination) door trim panels.

## 2.4. Test Methods

### Strength determination

All bonded specimens were tested in an Instron mechanical (Model 5565) tester at the strain rate of 10 mm/min. Five specimens per experimental point were tested.

### Adhesive Bonding

**Shear Strength:** The strength of the adhesive bonds was determined using single lap-shear specimens comprising 2 bonded coupons (50 x 25), see Fig. 2(a), with an overlap of 3 mm for rigid structural adhesives or 5–10 mm for elastomeric sealants. The narrow, 3 mm overlap was chosen for structural adhesives to avoid the substrate failure which commonly occurred with the standard-recommended 5–10 mm overlaps. Bonded specimens were clamped with bulldog clamps until full cure of adhesives. The specimens bonded with PU

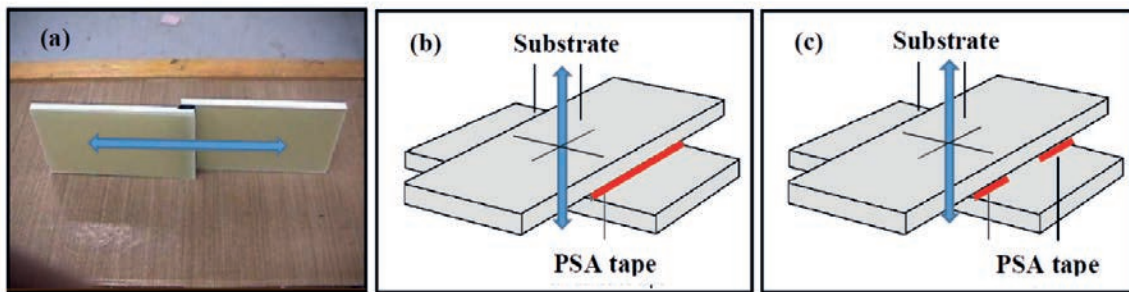


Fig. 2. Specimens for determining the strength of adhesion: (a) Lap shear specimens with cross-linkable structural adhesives; (b) cross-lap specimens: 3M VHB 4959/ 3 mm thick PSA (Pressure Sensitive Adhesive) tape; and (c) cross-lap 3M 4220/0.42 mm PSA tape (light-blue arrows indicate the principal stress direction during testing)

sealant were oven-cured at 70°C for 72 hours. A beaker of water was placed inside the oven to assist moisture cure of PU sealants.

**Tensile Strength for Self-adhesive Tapes and Sealants:** was determined using 50 x 25 mm cross-lap specimens, see Fig. 2(b) when using adhesive tape squares, 21 x 21 mm for VHB 4959 tape, and Fig. 2(c) when two strips of 3M/4220 automotive tape (5 x 25 mm) are used.

## 2.5. Painting and Assessment of Paint Adhesion

### 2.5.1. Specimen preparation and test procedure

All painting, including CPO primer application, was carried out using a robotic unit to produce a uniform paint film at the thickness required by the paint manufacturer and automotive companies. All coatings, CPO, basecoat, and clearcoat, were cured in accordance with industrial procedures.

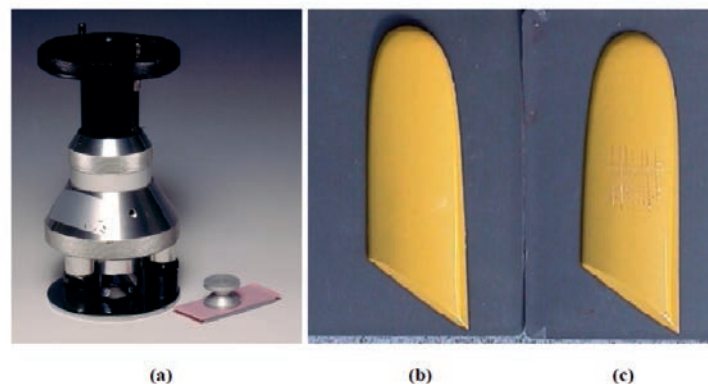


Fig. 3. (a) Elcometer adhesion tester and an ink-printed BOPP film specimen with a pull-off dolly bonded to the ink surface, (b) painted BSPM (Bodyside Protective Moulding), (c) cross-hatch tested painted BSPM, tested after 52-day QUV-B exposure

### 2.5.2. Adhesion assessment by pull-off test

The paint adhesion was assessed by pull-off test (ASTM D 4541-89) using an Elcometer (see Fig. 3) and an Instron tester. It has been recognised from previous work that the pull-off test using an Elcometer appears to provide more comprehensive information than the simple cross-hatch test (ASTM D 3359-93) for the purpose of unambiguous assessment of surface treatments for paint adhesion improvement. In the process of specimen preparation, a sandblasted clean aluminium dolly was adhesively bonded to the cured coating surface using a two-pack epoxy adhesive, before post-cure at 40°C (in convection oven) overnight. Prior to testing, a cut was made by a circular tool around the edge of the aluminium dolly to initiate a shallow crack-line through the paint.

### 2.5.3. Adhesion assessment by cross-hatch test

The quality of paint adhesion on automotive products (e.g., BSPM's) and on test plaques was alternatively assessed by the use of cross-hatch test (ASTM D 3359-95a: Measuring Adhesion by Tape Test). Prior to testing, a lattice pattern is cut through the paint layer using a cross-hatch cutting tool. A strip of high-grip self-adhesive tape (3M tape 8981) was subsequently pressed onto the cross-hatched area, followed by a rapid peel-off of the tape. The quality of adhesion is assessed in accordance with the automotive industry standards classification; ranking 10 – the best adhesion; level 8 – pass, and level 6 or below – failure.

## 2.6. Durability assessment

### 2.6.1. Adhesively Bonded Automotive Assemblies

#### (i) *Self-adhesive tapes (for BSPM bonding)*

All durability tests concerning self-adhesive tape adhesion based on tensile, lap-shear, or peel specimens involved an exposure and testing protocol described in Ford's Test Procedure: WSB-M3G 138-B, as well as a General Motors protocol. This involved pre-conditioning samples for 72 hours at  $23 \pm 2^\circ\text{C}$  prior to environmental exposure, as listed below, and tested between 1 and 4 hours after removal from the exposure environment.

- (i) **Room Temperature Aging**  
(no pre-conditioning for 72 hours)
  - 1 hour
  - 72 hours
- (ii) **Water Immersion**
  - 240 hours at  $32 \pm 1^\circ\text{C}$
- (iii) **Cycle Test (5 cycles consisting of)**
  - 8 hours at  $19 \pm 2^\circ\text{C}$
  - 16 hours at  $-7 \pm 2^\circ\text{C}$
  - 8 hours at  $38 \pm 2^\circ\text{C}$  and  $98 \pm 2\%$  RH
  - 16 hours at  $-7 \pm 2^\circ\text{C}$

- (iv) **Thermal Shock Test**
  - 16 hours at  $-7 \pm 2^\circ\text{C}$ . Then immediate immersion in water at  $70 \pm 2^\circ\text{C}$  for 5 minutes.
- (v) **Heat Aging**
  - 2 weeks at  $88 \pm 2^\circ\text{C}$
- (vi) **High Humidity**
  - 2 weeks at  $38^\circ\text{C}$  and  $98 \pm 2\%$  RH

#### (ii) *Polyurethane (PU) sealant (for BSPM bonding)*

All durability tests (fully cured PU adhesive: RT/72 hours) included the following exposures:

- **Room temperature aging:** 72 hours in a convection oven at  $70^\circ\text{C}$ .
- **Accelerated aging:** 2 weeks exposure at  $70^\circ\text{C}$ .
- **Humidity:** 1 week at  $38^\circ\text{C}/100\%$  RH: fully cured specimens were exposed to humid environment in a water bath (on a tray above the water level, at an angle of  $\sim 30^\circ$ ).
- **Water immersion:** 240 hours at  $38^\circ\text{C}$ : fully cured specimens were immersed in jars of distilled water, each jar placed in a water bath set at the above temperature for 10 days.
- **Cycle Test:** 2 cycles of the following exposure sequence: (1) 17 hours at  $-29^\circ\text{C}$ ; (2) 72 hours at  $70^\circ\text{C}$ ; (3) 24 hours at  $38^\circ\text{C}/100\%$  RH; (4) 7 hours at  $-29^\circ\text{C}$ ; (5) 17 hours at  $38^\circ\text{C}/100\%$  RH; (6) 7 hours at  $70^\circ\text{C}$ ; (7) 24 hours at  $38^\circ\text{C}/100\%$  RH.
- **Thermal Shock:** the lap shear specimens were subjected to the following exposure cycle: (1) 2 hours in  $20^\circ\text{C}$  water; (2) 2 hours at  $-29^\circ\text{C}$ , and (3) 15 sec in  $80^\circ\text{C}$  water.

### 2.6.2. Paint Adhesion

The following test protocol based on the GM Holden specification was used for the assessment of paint performance on painted exterior TPO components (BSPM and Bumper Materials):

- (i) **HN 1664 (Modified test 4.2/3)**  
**Water Immersion Test** (HN 0278 and HN 0279)  
240 hours exposure to water  $38 \pm 1^\circ\text{C}$
- (ii) **HN 1664 (Test 4.2/6)**  
**Petrol Resistance** (HN 0268; Method A)
- (iii) **PPG/CSIRO test**  
**Thermal Shock Test**  
(Modified Ford Procedure 3.8/WSK-M2P143-A)  
2 hours @  $-40^\circ\text{C}$   
5 minutes in  $70^\circ\text{C}$  water  
(3 repeats prior to adhesion testing)
- (iv) **HN 1664 (Test 4.2/2 and 4.2/3)**  
**Accelerated QUV Exposure** (ASTM G 53)  
Method b, High Temperature, UVB-313)  
Class II: Total exposure time: 1250 hours  
Cycle schedule: 8 hours UV at  $68^\circ\text{C}$   
4 hours condensing humidity at  $40^\circ\text{C}$

At the end of the above exposure, the painted TPO samples were retrieved and dried in ambient conditions for 1 hour, followed by either dolly bonding or cross-hatch testing. The subsequent assessment of paint adhesion was carried out following the identical procedure to that for dry paint adhesion, as described in Section 2.5. The average values of the strength of paint adhesion were determined from three to five replicates of specimens for each experimental condition.

### 3. Results

#### 3.1. Adhesive Bonding of Engineering Polyolefins and Other Plastics

The effectiveness of the ‘SICOR’ process for enhanced adhesion of LDPE, PP, HDPE, and UHMPE was assessed by lap shear tests. Fig. 4 compares the bond strengths of these polymers untreated and surface treated with corona discharge, flame, and the ‘SICOR’ process incorporating surface amine groups. It is seen

that the SICOR process always leads to a significant strength increase in comparison with standard corona discharge or flame treatment. Significant changes are also observed in the fracture mechanism that changes from 100% adhesive delamination in untreated and corona or flame treated polyolefins, to 100% cohesive failure within the substrate or adhesive for the ‘SICOR’ process with amine grafting.

The advantages of ‘SICOR’ process are even more obvious after wet exposure, i.e. immersion for 1 week and one month in hot water (60°C). Graphs in Fig. 5 shows these results for bonds involving LDPE bonded with Loctite 406 cyanoacrylate adhesive. The corona only treated specimens lack resistance to water immersion and delaminate within one day. The strength retention of the bonds with NH<sub>3</sub> plasma treated LDPE after one month of hot water immersion is about 60%. In contrast with that, about 90% strength retention is achieved with the joints comprising SICOR-treated LDPE, exhibiting 100% cohesive failure within the substrate. The small decrease in the strength is associated with the plasticizing effect of hot water on the LDPE.

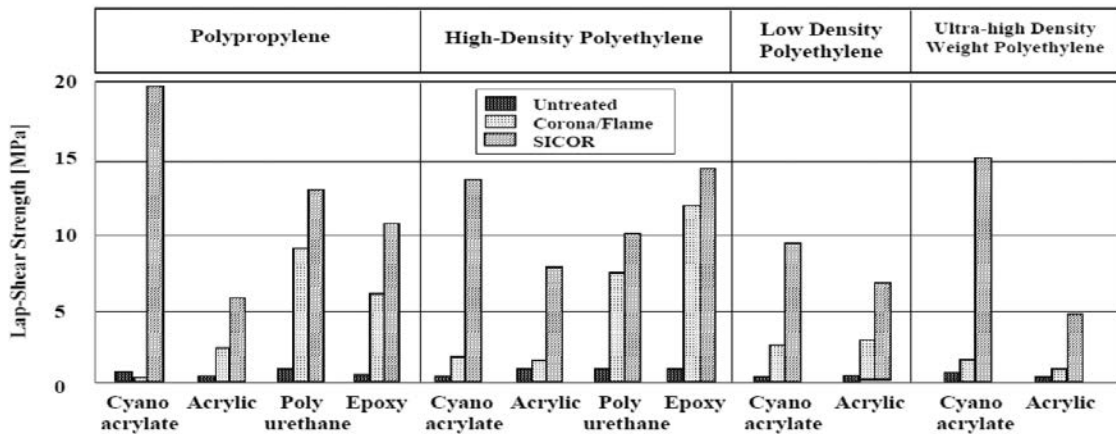


Fig. 4. Lap shear strengths of untreated and surface treated polymers bonded with a cyanoacrylate (Loctite 406), an acrylic (F241), an epoxy (Araldite 138) and a polyurethane (Tyrite 7520) adhesive [6]

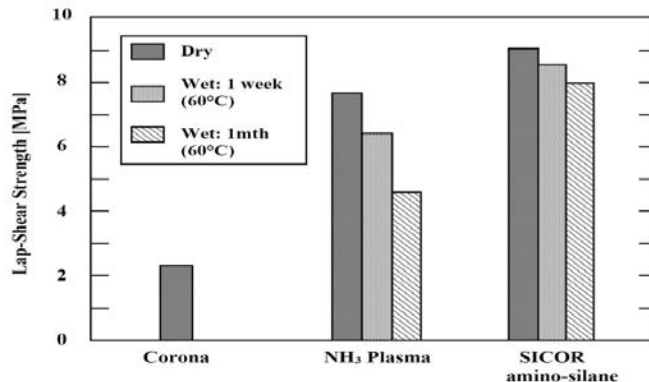


Fig. 5. Lap-shear strength of LDPE/cyanoacrylate joints in dry and wet environments [6]. Wet adhesion assessed after 1 week and 1 month immersion in 60°C water

### 3.2. Adhesive Bonding of Automotive TPO's

#### 3.2.1. BSPM bonding with self-adhesive tapes

Table 1 demonstrates the results of bonding BSPM grade TPO using the 3M VHB tape 4220, after accelerated exposure weathering of bonded specimens (see test protocols detailed in Section 2.6).

The results in Table 1 demonstrate the following: (i) untreated and flame-treated substrates fail predominantly by delamination between the tape and substrate, and (ii) flame treatment results in significant increase of the bond strength over untreated substrate. However, the failure mode remains predominantly 70 to 80% AF, i.e. almost complete tape delamination; (iii) SICOR surface

treatment results in not only increased bond strength, but also in 80 to 100% CF within the tape. Therefore, the tape cohesive strength becomes the limit to the overall performance of the assembly.

One of important areas of the application of adhesive bonding in the automotive industry is the bonding of various decorative components to painted body panels or to bumper bars. GM Holden Australia tested the adhesion of polypropylene bodyside moulding strips on a Holden Caprice, using the CSIRO technique. The durability assessment, in addition to the protocol outlined in 2.6, also involved running test vehicles through over 40,000 km on a variety of road surfaces, including 6,000 km of very rough terrain.

**Table 1. Strength of Adhesion [MPa] in tensile mode between Corton BSPM and 3M Tape No. 4220, and Failure Mode of the bond (% of Cohesive Failure [CF] in the Tape or % of delamination [AF] between the Tape and BSPM) [7]**

BSPM Surface Treatment	Exposure Type													
	RT Aging 1 hour		RT Aging 72 hours		Heat Aging		Humidity		Water Immersion		Cycle Test		Shock Test	
	MPa	CF/AF	MPa	CF/AF	MPa	CF/AF	MPa	CF/AF	MPa	CF/AF	MPa	CF/AF	MPa	CF/AF
Untreated	0.45	0/100	0.5	0/100	0.55	0/100	0.29	0/100	0.32	0/100	0.53	0/100	0.52	0/100
Flame	0.49	0/100	0.65	16/84	0.97	9/91	0.46	60/40	0.44	30/70	0.68	20/80	0.61	0/100
SICOR	0.61	98/2	0.70	90/10	1.10	80/20	0.46	100/0	0.41	100/0	0.71	100/0	0.61	68/32

#### 3.2.2. BSPM bonding with polyurethane sealant

The BSPM grade TPO assessed was Corton polypropylene blend (PolyPacific/Australia) filled with 13% talc. Polyurethane sealant Betaseal 55402 was

used for bonding. After bonding, the specimens were subjected to a range of tests specified in Section 2.6.1 (ii). The results in Table 2 present the results of tensile strength of the bond and the failure mode.

**Table 2. The performance of BSPM Corton substrate bonded with PU sealant (Betaseal 55402) subsequent to the durability exposure protocol specified in Section 2.6.1 Bond strength in [MPa], and percentage of delamination between substrate and PU adhesive [%AF]**

Treatment	72hr Aging at RT		2 weeks at 70°C		Humidity (38°C/100%RH)		Water Immersion (240hr at 38°C)		Cycling		Thermal Shock	
	MPa	%AF	MPa	%AF	MPa	%AF	MPa	%AF	MPa	%AF	MPa	%AF
Flame	3.6	100	3.2	100	1.9	100	1.5	100	3.4	100	1.4	100
SICOR	6.2	20	6.4	27	4.2	18	4.2	18	5.3	17	4.3	18

The results in Table 2 demonstrate the following: (i) assemblies with flame-treated substrates fail by 100% delamination between the sealant and substrate, and (ii) SICOR surface treatment results in not only increased bond strength, but also leads to cohesive failure within the sealant. Therefore, the sealant's cohesive strength becomes the limit to the overall assembly performance.

### 3.3. Painting Automotive TPO Substrates for Exterior Components

Ford bumper bar TPO (PP/EPDM blend) was surface treated using the following processes:

- (i) Flame treatment: speed: 60m/min; flame tip – TPO distance: 15mm; O<sub>2</sub> excess: 0.4%; 2 flame passes; flame energy output: 35 kW @ 200mm burner.

- (ii) Flame treatment and industry approved CPO primer (Hyperprime PPG No: 499-45848).
- (iii) SICOR: Flame as in (i) and selected graft chemical diluted in water.

After treatments (i) to (iii) above, the substrates were painted using PPG Heron White basecoat and clear coat, identical to those listed in Section 2.3. Paint adhesion performance was assessed after the following exposures: dry, and with 10 days immersion in 70°C water (see Fig. 6).

As seen in Fig. 6(a), after 10 days immersion in 70°C water, the SICOR process for bumper bar grade

TPO treatment shows better performance than flame and CPO primer. The failure mode for the SICOR-treated samples was 100% cohesive failure within the substrate, whilst 70% of the samples treated with the CPO demonstrated delamination between the paint and the substrate. Figure 6(b) depicts fracture surfaces after dolly pull-off tests subsequent to 10 days immersion in 70°C water and bond strength in MPa. It also highlights the variance experienced using the current industry-approved pre-treatment process and clearly displays the predominantly cohesive failure within the substrate for the SICOR treated samples.

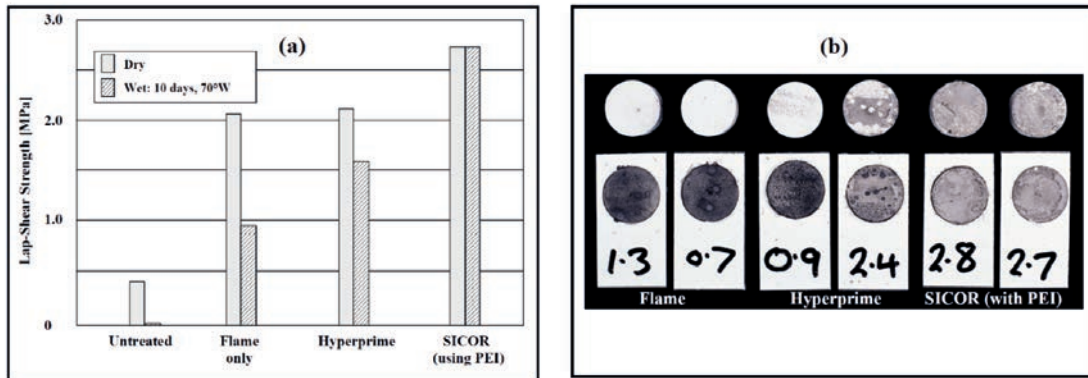


Fig. 6. Paint adhesion results (dolly pull-out tests) for flame, chlorinated primer and SICOR-treated bumper-grade TPO after ‘dolly pull-out’ tests : (a) strength of adhesion [MPa], and (b) appearance of interfacial fracture surface (between substrate surface and paint). Note 100% paint delamination on flame-only treated substrate and 100% cohesive failure within polymer for SICOR-treated substrate

## 4. Production Trials

### 4.1. BSPM Bonding

A typical BSPM grade material used throughout the development and industrial tests was a talc filled PP ((Corton1054/2 HS: Natural (no pigment); Black and Grey, and all Montell polymers were supplied by PolyPacific/Australia)), subsequent to passing all GM

Holden performance requirements (see Section 2.6.1), the SICOR-modified BSPM have been in production since 1998 and are installed on all GM-Holden vehicles in Australia. See Fig. 7 for illustration of the procedure concerning the following: (a) adhesive bonding of TPO-based BSPM to the surface of painted vehicle body panels, and (b) the quality of adhesion for TPO substrates without treatment and after surface oxidation (corona discharge or flame) or SICOR process with PEI connector molecules.

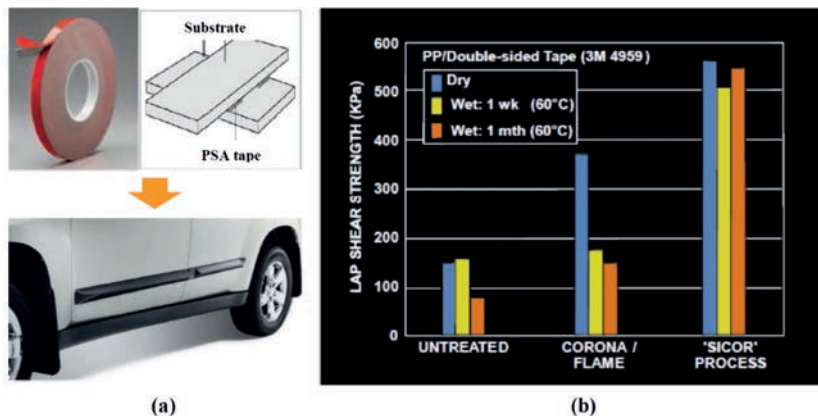


Fig. 7. (a) adhesive bonding of TPO-based BSPM to the surface of painted vehicle body panels, and (b) the quality of adhesion for TPO substrates without treatment and after surface oxidation (corona discharge/flame) and SICOR (with PEI connector molecules)



## 4.2. BSPM Painting

Bodyside protective mouldings (BSPM's) for commercial production and painting trials were injection moulded using PD0046.40 material supplied by CompCo/Melbourne. All BSPM's were SICOR treated on the industrial SICOR unit currently used for BSPM treatment for bonding (see Section 4.1 above). After the treatment, all products were commercially painted using the following PPG paints currently in use on General Motors Holden vehicles in Australia, as listed in Section 2.2. All painted BSPM's were subsequently subjected to an accelerated exposure protocol described in Section 2.6.2. Cross-hatch adhesion testing (Section 2.5.3) revealed that all BSPM's exhibited excellent adhesion with the level of adhesion ranked 10. Figure 3(c) illustrates an example of a painted BSPM treated with the SICOR process prior to painting (photograph depicts BSPM with and without cross-hatch adhesion tests after 52 days QUV exposure).



**Fig. 8. SICOR treatment of automotive TPO instrument panel (IP): (a) flame treatment prior to spray-application of PEI-based primer, and (b) IP after vacuum wrapping**

## 4.4. Door Trim Panels: Substrate Lamination and Wrapping With Flexible Coverstock

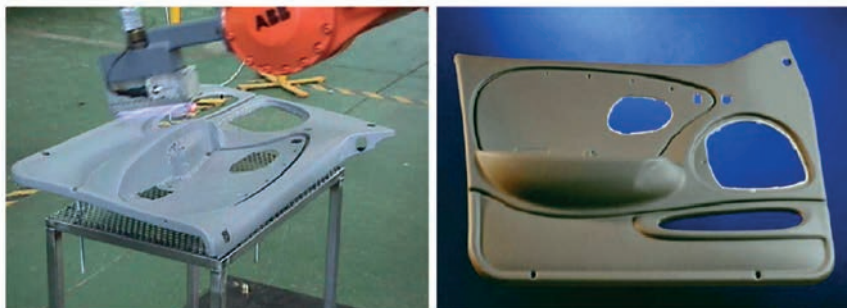
Door trim panels were injection moulded using Jazz 012/4 TPO blend (recycled TPO from PolyPacific/Melbourne). Surface modification was carried out using robotized (ABB robot) flame treatment and spray

## 4.3. Instrument Panels: Substrate Lamination and Wrapping With Coverstock

Instrument panels were injection moulded using Extron PDR 3039 HS7386 (PolyPacific Melbourne) material. Surface modification was carried out using robotized (ABB robot) flame treatment (see Fig 8a) and spray application of a dilute solution of graft chemical. All substrates were subsequently vacuum-wrapped with a PVC skin/PE foam coverstock material applied onto a spray-applied polyurethane adhesive, see Fig. 8(b).

In order to assess the quality of adhesion and product performance, instrument panels were subjected to accelerated exposure protocol specified in Section 2.6.1 [(i) to (vi)]. The tests revealed that all performance requirements were satisfied with 100% cohesive failure within the foam occurred on product surfaces (the face and all back-wrapped surfaces along the edges).

application of a dilute solution of graft chemical. All substrates were subsequently vacuum-wrapped with a PVC skin/PE foam coverstock material applied onto a spray-applied polyurethane adhesive. Figure 9(a) demonstrates the SICOR treatment of the door trim panel prior to vacuum wrapping, and Fig. 9(b) shows the panel after the lamination/wrapping cycle.



**Fig. 9. (a) SICOR treatment of PP door trim panel prior to vacuum wrapping, and (b) door trim panel after wrapping/lamination with PVC skin/PE foam coverstock material**

In order to assess the quality of adhesion and the overall product performance, door trim panels were subjected to accelerated exposure protocol specified in Section 2.6.1 [(i) to (vi)]. All performance requirements were satisfied. In all cases, 100% cohesive failure within the foam occurred on all surfaces of the product (the face and back-wrapped surfaces along entire edge).

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## 5. Processing speed and installation flexibility

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The SICOR process can be easily integrated into existing manufacturing systems, and it can be used as an on-line system allowing treatment speeds of up to 300 m/min. It can be also used for the treatment of complex 3-dimensional systems (e.g., bumper bars, or instrument panel components) using a robotic unit with a line speed of up to 60–85 m/min.

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## Conclusions

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The process discussed in this paper effectively treats 2-dimensional and 3-dimensional objects.

A surface engineering technique for polymers comprising surface oxidation (e.g., by flame or corona discharge treatment, etc.) and organo-functional graft chemical deposition provides a very effective means for enhancing the adhesion of engineering plastics and organic coatings with a range of typical engineering adhesives, elastomeric sealants, and organic coatings.

The comparative study on the process effectiveness involving flame treatment, corona discharge, SICOR process (flame or corona discharge + graft chemicals), and various plasma treatments, indicates that the process developed and described in this paper demonstrates four key advantages over current surface treatment technologies: (i) It provides significantly enhanced bond adhesion strength and durability when compared to current methods of polymeric substrate pre-treatment; (ii) It provides significant cost savings, comparative with all currently known processes, by allowing the use of cheaper materials and more efficient processes; (iii) The process meets global environmental policies on the elimination of ozone-depleting substances, including solvents and chlorine-based materials; and, (iv) The process can be easily integrated into existing manufacturing systems, treating at speeds of up to 300 m/min.

The technology has been extensively tested, demonstrating excellent results on normally difficult to bond homopolymers and blends based on polyethylene, polypropylene, polyvinylidene fluoride (PVDF), polyacetal, and other plastics.

Validation tests carried out on a range of adhesively bonded substrates have proven the ability of the SICOR process to meet the technical specifications relevant to adhesively bonded automotive components (Ford, GM Holden, Toyota and Mitsubishi), and those relevant to structural bonding with sealants in the automotive and building and construction industry.

The technology discussed in this paper opens up new opportunities for various industries, including the automotive industry, due to the following: (i) Enabling more efficient bonding and painting of the currently used TPO's as well as other materials not previously used due to inherent adhesion problems, and (ii) Enabling more efficient and safe design and construction with structural sealants and self-adhesive tapes due to drastically improved quality of adhesion.

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## References

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1. Gutowski, W., Wu, D.Y., Li, S., 'Surface Treatment of Polymers', Australian Patent No. 680716 (IP Australia, Sydney, Australia, 1998).
2. Gutowski, W., Wu, D.Y., Li, S., 'Surface Treatment of Polymers', United States Patent No. 5,879,757 (US Patent and Trademark Office, Washington, DC, USA, 1999).
3. Gutowski, W.S. and Pankevicius, E.R., 'A novel surface treatment process for enhanced adhesion of ultra-high modulus polyethylene fibres to epoxy resins', *Composite Interfaces* **1** (2) (1993) 141–151.
4. Gutowski, W.S., Wu, D.Y. and Li, S., 'Surface silanization of polyethylene for enhanced adhesion', *Journal of Adhesion* **43** (1993) 139–155.
5. Wu, D.Y., Li, S., Gutowski, W.S., 'Surface Treatment of Polymers', United States Patent No. 5,922,161 (US Patent and Trademark Office, Washington DC, USA, 1999).
6. Gutowski, W.S. and Wu, D.Y., 'Effective surface treatments of polymeric materials for bonding with adhesive and sealants', in 'Proceedings of Adhesives and Sealants Seminar, Melbourne, Australia, 21 October 1993' (Society of Automotive Engineers (SAE), Melbourne/Australia, 1993) 1–6.
7. Filippou, C., CSIRO Internal Report (Commonwealth Scientific and Industrial Research Organisation, Melbourne, Australia, 1998).
8. Wu, D.Y., Test Results for Validation of Paint Adhesion Performance of SICOR-treated Exterior Plastic Components. CSIRO Internal Report, Melbourne, Australia. November 1998.
9. Wu, D.Y. and Morehouse, M., CSIRO Internal Report (Commonwealth Scientific and Industrial Research Organisation, Melbourne, Australia, 1998).