

Wojciech S. GUTOWSKI*, Con FILIPPOU, Sheng LI

CSIRO Manufacturing Flagship, Industrial Interfaces Group, Melbourne, Australia

* Corresponding author: Voytek.Gutowski@csiro.au

MULTIFUNCTIONAL INTERPHASES IN ELECTROSTATIC COATING OF ELECTRICALLY NON-CONDUCTIVE MATERIALS

© 2018 Wojciech S. Gutowski, Con Filippou, Sheng Li

This is an open access article licensed under the Creative Commons Attribution International License (CC BY)

<https://creativecommons.org/licenses/by/4.0/>**Key words:** plastics, polyolefins, polymeric composites, surface conductivity, powder coatings, adhesion.

Abstract: Solvent-based or waterborne coatings commonly used in surface finishing of plastic or composite-based products exhibit very low spray transfer efficiency, typically not exceeding 30–35%. Powder coatings, an attractive 100% solvent-free alternative technology, achieve up to 95–98% material utilization. However, they require electrostatic deposition of charged powder particles and hence can only be used on inherently conductive, e.g., metallic components. Overall, the key barriers for wide application of powder coating technology in plastics surface finishing are the non-conductive surfaces of plastics, inadequate adhesion to commodity plastics, and frequently the absence of low-temperature powder resins. This paper presents practical aspects of technology facilitating successful electrostatic powder coating of automotive and commodity plastics achievable through surface-grafted arrays of amino-functional molecules exhibiting inbuilt electron conductivity. This results in a 10^8 -fold increase in surface conductivity of polymers combined with up to a 1000-fold increase of the strength of adhesion between adhesively bonded or surface-coated assemblies in comparison with unmodified substrates to the point of achieving 100% cohesive fracture of substrates. Industrial-scale technology trials using full size PP-based automotive components carried out by CSIRO and Dulux in a commercial powder coating facility demonstrated the suitability of this technology for industrial applications targeting the substitution of the current liquid paints by zero-waste powder coatings.

Wielofunkcyjne międzyfazy dla elektrostatycznego malowania materiałów elektrycznie nieprzewodzących

Słowa kluczowe: polimery, poliolefiny, kompozyty polimerowe, przewodność powierzchniowa, malowanie proszkowe, adhezja.

Streszczenie: Rozpuszczalnikowe lub wodnorozpuszczalne powłoki dekoracyjne i ochronne oraz farby powszechnie stosowane w wykańczaniu powierzchni wyrobów z tworzyw sztucznych lub kompozytów wykazują bardzo niską skuteczność przenoszenia natryskowego, zwykle nieprzekraczającą 30–35%. Powłoki proszkowe (atrakcyjna 100%-bezzroczalnikowa technologia) pozwalają na podniesienie efektywności użycia materiału do 95–98%. Wymagają one jednak elektrostatycznego osadzania elektrycznie naładowanych cząstek proszku, w związku z czym ich zastosowanie ogranicza się do naturalnie elektroprzewodzących materiałów takich jak metale. Generalnie biorąc, głównymi barierami dla szerokiego zastosowania technologii powlekania proszkowego w wykończeniu powierzchni tworzyw sztucznych są: nieprzewodzące powierzchnie z tworzyw sztucznych, nieodpowiednia przyczepność powłoki do wyrobów z tworzyw sztucznych, a często też brak niskotemperaturowych żywic proszkowych. W artykule przedstawiono praktyczne aspekty technologii ułatwiającej elektrostatyczne lakierowanie proszkowe wyrobów polimerowych dla przemysłu samochodowego oraz generalnego przeznaczenia osiągalne dzięki łańcuchom molekularnym z aminowymi grupami funkcyjnymi wykazującym wbudowane przewodnictwo elektronowe. Powoduje to zwiększenie przewodnictwa powierzchniowego polimerów zwielokrotnione w stopniu sięgającym do 10^8 w porównaniu z materiałem nieobrobionym, które połączone jest z równoczesnym 1000-krotnym wzrostem wytrzymałości adhezji pomiędzy elementami klejowymi, lub substratem a farbą lub powłoką dekoracyjno-ochronną (również w porównaniu z substratami niezmodyfikowanymi), które wiąże się często z osiągnięciem 100% pęknięcia kohezijnego materiału malowanego lub klejonego. Próby technologiczne w skali przemysłowej z wykorzystaniem pełnowymiarowych elementów samochodowych opartych na polipropylenie (PP) przeprowadzonych przez CSIRO i Dulux/Australia w komercyjnych lakierniach proszkowych, wykazały przydatność tej technologii do zastosowań przemysłowych, których celem jest zastąpienie obecnych farb płynnych bezodpadowymi (bezzroczalnikowymi) pokryciami proszkowymi.

1. Principles of electrostatic powder-coating technology

1.1. Powder coating transfer

Powder coating is a dry surface finishing process utilising micro-sized particles of pigmented resin, which are electro-statically charged and deposited on the coated product surface. Due to electrostatic transfer of charged particles, all powder-coated products have to be electro-conductive, thus limiting the use of powder coating to surface finishing of metallic products. Conversely, non-conductive materials such as plastics, WPCs, Wood-Plastic Composites, and other wood-based products require the application of conductive primers to facilitate electrostatic coating deposition.

Figure 1 schematically illustrates the principles of electrostatic powder-coating technology. An ionised air zone is formed around the tip of corona discharge electrode at the electrostatic gun nozzle outlet. This imparts a negative electrical charge on all powder

particles that consequently form a fluidised particulate cloud in which all identically charged particles repel each other. A stream of pressurised air propels charged particles towards the grounded electro-conductive substrate.

1.2. Interactions of single molecules of graft chemicals with a polymeric substrate

This work focuses on systems providing combination of surface conductivity and adhesion promotion through the use of selected molecules containing simple aliphatic amine groups such as polyethelene imines (PEI) and amino-silanes (see Fig. 2). When grafted to polymers pre-oxidized by corona discharge, plasma, UV radiation, or flame, these categories of molecules facilitate the control of surface architecture at polymer interfaces and turn their chemically inert and non-conductive surface into a good surface conductor whilst simultaneously providing excellent adhesion of coatings, adhesives, printing inks, and biomaterials, including live cells proliferation [1–5]. Oxygenated species, e.g., COOH

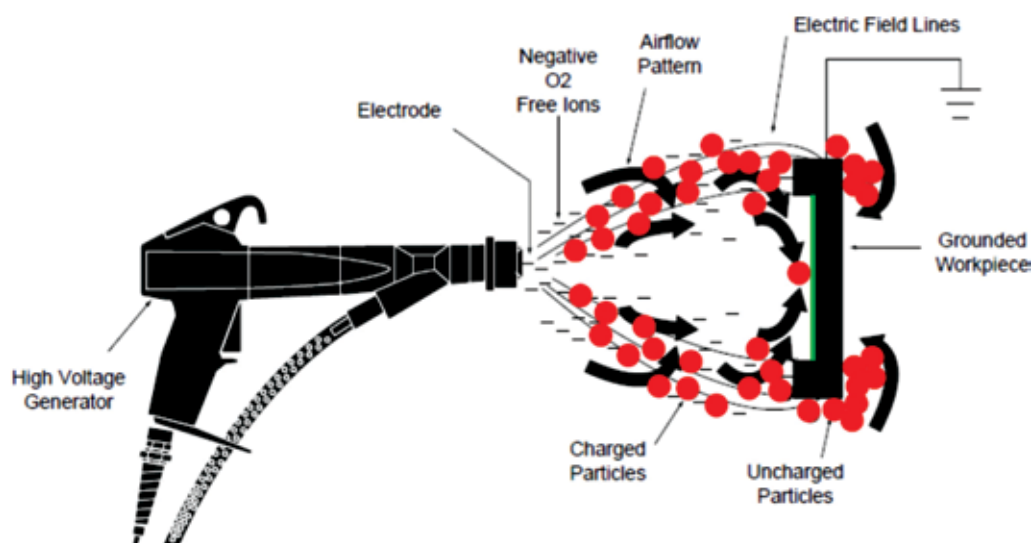


Fig. 1. Schematics of electrostatic powder-coating discharge and deposition

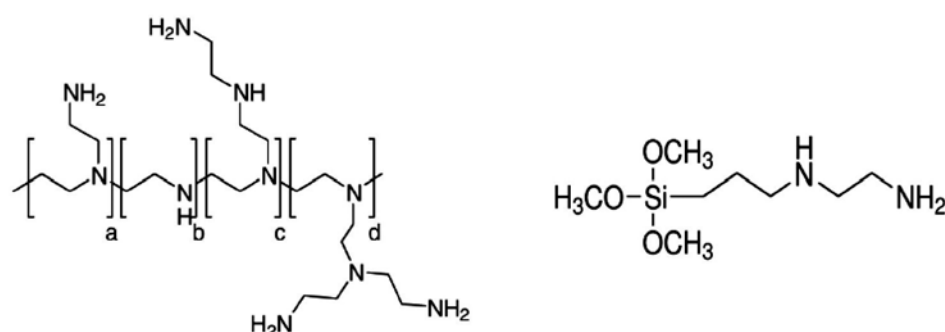


Fig. 2. Chemical structure of graft molecules used in this work: (a) Polyethyleneimine, and (b) N-(2 aminoethyl)-3-aminopropyl-trimethoxysilane: Z-6020 (Dow Corning)

or OH created by mild surface oxidation form a dense 2-dimensional array of reactive sites forming a scaffold for the attachment of PEI or amino-silane molecules through their functional groups bonding through either hydrogen, ionic, or covalent bonds, as illustrated in Fig. 3.

To elucidate the mechanisms of the interactions of individual molecules of cationic PEI with the surface of negatively charged COOH sites, atomically smooth Muscovite mica was used as an analogue substrate model. This facilitated the simulation of interactions of PEI molecules with oxidized surface of polymers such as PP or PE including the elucidation of the mechanisms of spatial architecture control of resultant interphases by modelling programs utilising molecular and quantum mechanics in a DMol3 environment (Materials Studio, Accelrys). Figure 4 illustrates selected consecutive stages of the adsorption of PEI macromolecules applied onto the surface of negatively charged model substrate at a neutral charge ($\text{pH} \approx 10.3$ /un-protonated state) or as 75% protonated molecules (solution at $\text{pH} \approx 6.0$). It is clearly seen that increasing electrostatic contribution through

protonation of PEI leads to significant conformational and mechanistic gains attained through the increased aspect ratio of adsorbed molecules, i.e.: (i) an increased footprint of docked molecules, (ii) an increased height of the vertically stretched strand, and (iii) an increased, i.e. almost doubled number of hydrogen bonds for protonated PEI resulting from increased electrostatic interaction bringing the molecular groups into closer contact with the substrate surface. Conformational gains illustrated in Fig. 4 were experimentally confirmed by imaging PEI macromolecules on mica in air, using advanced non-contact AFM in combination with a high aspect ratio (1nm radius) tip.

1.3. Imparting surface-conductivity and adhesion promotion to polymeric substrate surface

the inherent lack of bulk and surface conductivity of polymers can be, to a limited extent, overcome by the use of conductive polymer blends containing adequate

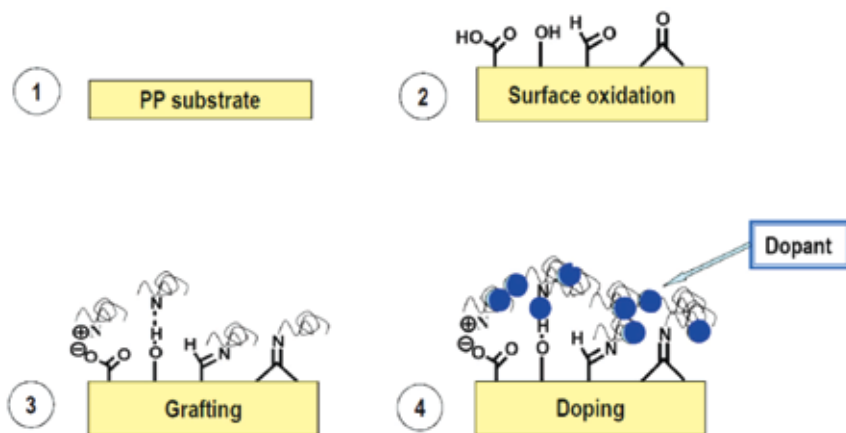


Fig. 3. Schematics of surface grafting of PEI molecules onto surface-oxidized polymers, e.g., polyolefins

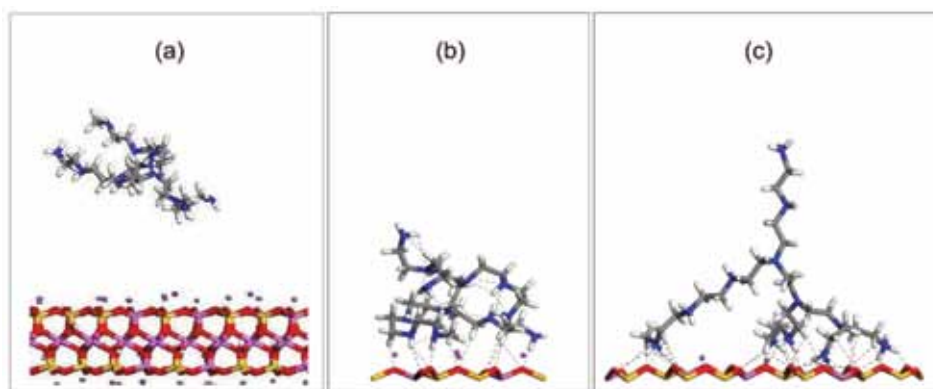


Fig. 4. Adsorption and surface conformation of unprotonated ($\text{pH} 10.3$) and highly [75%] protonated (at $\text{pH} 6.0$) PEI macromolecules on the surface of negatively charged model substrate. (a) initial condition, in aqueous environment; (b) un-protonated PEI molecule; (c) highly protonated, adsorbed, PEI molecule [5]

levels of conductive fillers, or by the use of conductive primers applied prior to powder coating deposition. These can be achieved by the addition of conductive carbon black (10–16%), carbon nano-tubes (2–5%), or other additives. However, the above solutions are not sustainable due to the high material cost and the high VOCs content in commodity conductive primers.

The technology outlined in this paper facilitates the use of electrostatic powder coating in the surface finishing of commodity injection-moulded plastic components which are not inherently conductive.

Figure 5 provides a schematic illustration of the principles of this technology comprising the formation of an electro-conductive surface on the non-conductive product surface which simultaneously provides excellent adhesion between the plastic substrate and micro-sized powder coating resin. This is achieved by the spray application of a nano-thin layer of electro-conductive molecules (item [2] in Fig. 5(a)) onto the surface of flame-treated non-conductive plastic facilitating uniform conductivity between adjacent molecules.

The uniformly charged particles electro-statically attracted to the entire surface of the now conductive substrate where they self-assemble as uniform films.

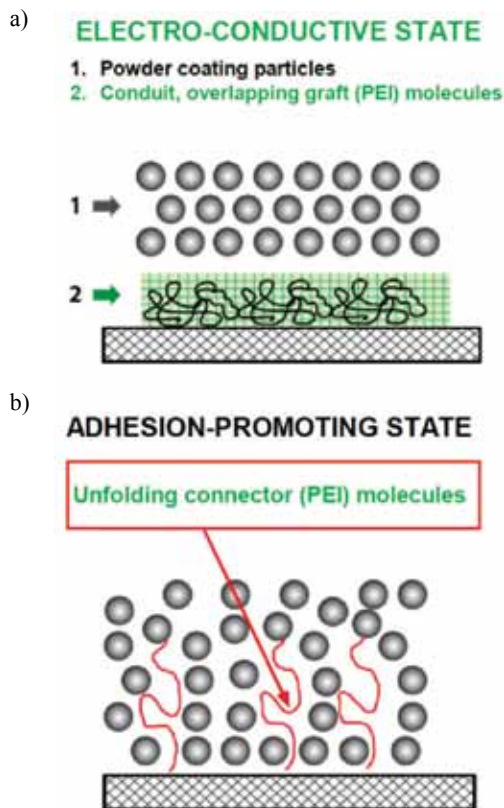


Fig. 5. Schematic principles of CSIRO polymer surface modification system for surface electro-conductivity and adhesion enhancement: (a) electro-conductive state; (b) adhesion-promoting state: unfolded molecules penetrating into a layer of powder coating particles

After this, once the powder coated product enters high-temperature zone of the curing oven (exposure to heat energy), the following takes place: (1) micro-particles of powderized coating resin melt and are self-levelling when heated to the appropriate temperature; (2) the graft molecules (chemically attached to the surface) unfold from the mutual entanglement (initially providing excellent surface conductivity), and (3) penetrate into the coating, resulting in excellent coating adhesion, and ultimately, (4) are cross-linked into a tough coating film.

2. Experimental

2.1. Surface conductivity measurements

Measurements of surface conductivity were carried out using a Keithley Electrometer 6517A with the Resistivity Test Fixture 8009 attachment. Six conductivity measurements are taken, discarding the initial two measurements as the current reaches a steady-state, to determine the conductivity of each sample. Relative humidity and ambient temperature are also monitored during all conductivity measurements. Multiple replicates are tested for each set of treatment conditions and chemical formulations.

2.2. Powder coating application and cure

The surface modified substrate samples were powder coated in CSIRO laboratories using a lab-scale fully robotized coating facility depicted in Figure 6, comprising a spray booth and an ITW Gema electrostatic powder gun with an electronic control unit. The consistency of the powder transfer rate and thickness is controlled through the use of a robot facilitating constant and repeatable coating conditions, e.g., (a) coating speed, (b) sample-to-spray gun distance, etc.



Fig. 6. Robotised electrostatic powder coating facility at CSIRO laboratories

A metal plaque is always used as a reference material to facilitate rapid assessment of the quality of the powder coating of surface-treated polymer or wood-plastic composite or solid wood versus that of a metallic substrate. Coated samples are baked and conditioned prior to tests as specified by the coating suppliers.

2.3. Coating performance assessment protocols

The performance of powder coating on all substrates has been assessed in accordance with standard procedures used for coated polymeric products by the automotive industry, i.e.: General Motors- Holden (GM), Specification HN-2184: Paints adhesion test protocol, comprising the following:

a) Initial adhesion:

- Cross-hatch cutting in the coating: 6 parallel cuts spaced at 2 mm
- Adhesion peel test as per HN 0279. Performance – minimum rating of 8 (rating identical to #1 in AS 3715 (2002) – Metal finishing).

b) After accelerated exposure: protocol HN-2184, as follows:

- Cross-hatch cutting in the coating prior to accelerated exposure protocol [as per HN 0279: identical to AS/NZ Standard 408.4 (2004)]
- 72 hours humidity exposure as per HN 0256
- 1 hour immersion in distilled water as per HN 0278
- Drying for 1 hour at room temperature (after surface wipe by a tissue)
- Adhesion peel test as per HN 0279. Performance – minimum rating of 8 (rating identical to AS 3715 (2002) – Metal finishing).

2.4. Assessment of the durability of powder coated plastics

The GM exposure protocol simulating a 3-year equivalent of weathering at Allunga Exposure Laboratory (Queensland, Australia) or in Florida, USA:

- HN 1664 (Test 4.2/2 & 4.2/3): Accelerated Exposure – QUV
ASTM G 53, Method b, High Temperature, UVB-313 and 340 nm UV tubes) / HN 0276

Total exposure time: 1250 hours (equivalent to approx. 3-year service)
Cycle schedule: 8 h UV at 68°C / 4 h condensing humidity at 40°C

3. Results

3.1. Surface Conductivity Enhancement

As illustrated in Fig. 7, the surface conductivity of thin PEI films fabricated through adsorption on mica

from 0.0001–10% solutions is significantly improved with increasing PEI concentration. It can be also seen in Figure 8 that the use of protonated PEI improves surface conductivity of mica by approximately 1.5 orders in magnitude. This is due to significantly increased charge carrier (protons) density as well as lower distance between accordingly stretched surface-bound branches of neighbouring PEI molecules, as illustrated in Figure 4 above.

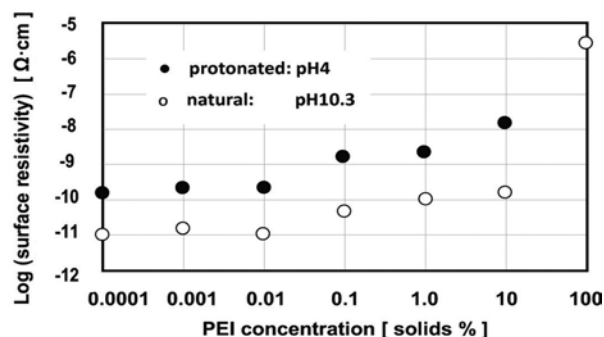


Fig. 7. Surface conductivity of thin films of PEI [MW 800] on Muscovite mica

Our earlier work [1] demonstrated that molecules of polyethyleneimine are permanently grafted to oxidised surfaces of polymers through the reaction of pendent amine groups with surface COOH groups created by oxidation by corona discharge, plasma, or flame treatments.

Owing to permanent attachment of individual PEI molecules in the form of highly ordered surface structures [see Figure 4(c)], a stable chemically bonded film [10–20 nm] of solid polyelectrolyte is built on surfaces of polymeric materials. Spray application or commodity printing processes are suitable for the application of low concentration water-based PEI solutions, typically not exceeding 0.5–1.0%. This, in turn, effectively converts non-conductive polymers, characterized by very high surface resistivity in the range of 10^{-16} – 10^{-14} Ω·cm into highly surface-conductive materials exhibiting long-term stable surface resistivity at the level of 10^{-8} – 10^{-7} Ω·cm, as illustrated in Figure 9. This constitutes an approximately 8 orders of magnitude increase in surface conductivity due to the creation of a conduit for electron transfer across a dense surface array of protonated amine groups of PEI.

Low surface resistivity (10^{-8} – 10^{-7} Ω·cm) of chemically grafted PEI-based molecular brushes facilitates applications of such modified polymers in areas requiring excellent adhesion promotion combined with surface conductivity. One of such applications is electrostatic coating of polymers by wet paints or powder coatings for exterior applications, as shown in Figure 8. Such electro-statically assisted transfer of coating particles drastically improves the coating's

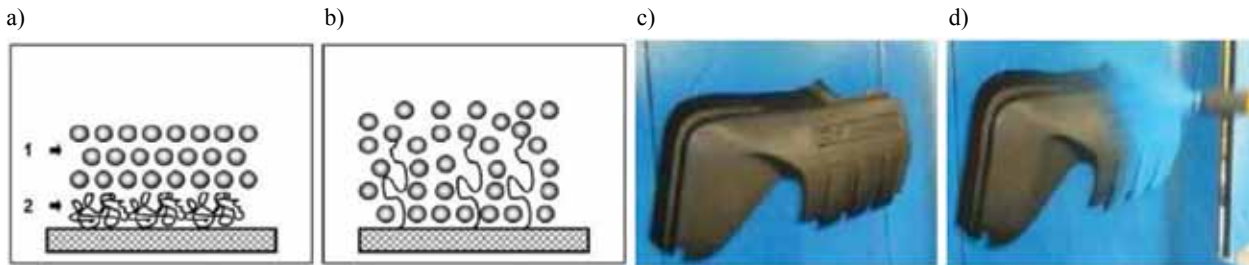


Fig. 8. Schematics of polymer surface modification by protonated PEI molecular brush for surface conductivity and adhesion enhancement: (a) electro-conductive surface state; (b) adhesion-promoting surface state: graft molecules unfold upon heat impulse (in powder coating) or on contact with wet paint (wet spray painting), subsequently penetrating into a layer of wet paint or powder particles; (c) PP-based engine block cover with PEI electro-conductive nano-coating, and (d) powder coating: excellent electrostatic transfer of powder particles (20 μm) onto the surface-conductive polymeric product

transfer effectiveness in comparison with unassisted applications from approximately 40 to 60% in wet painting, and reaching approximately 95–98% in powder coatings, which is a process that is not applicable for commodity, i.e. non-conductive polymers. It needs to be noted that powder coating completely eliminates VOCs emission, solid wastes, and all water wastage due to the elimination of the need for a water curtain catching wet paints overspray in commodity painting processes.

The process illustrated in Fig. 8 has been industrially trialled for automotive, construction, and household appliance applications requiring a surface finish suitable for exterior applications associated with the need for high-durability, high scratch resistant coatings.

As highlighted above, data in Figure 9 demonstrate significantly improved surface conductivity (i.e. reduced resistivity) of polypropylene blends after surface grafting of conductive adhesion promoter molecules: ‘1’ and ‘2’. It is seen that surface conductivity of PP modified by molecules ‘2’ is approximately 900,000 times better than that of the untreated or flame-treated polymer. Figure 10, in turn, demonstrates the effectiveness of the powder transfer to the surface of polypropylene blends.

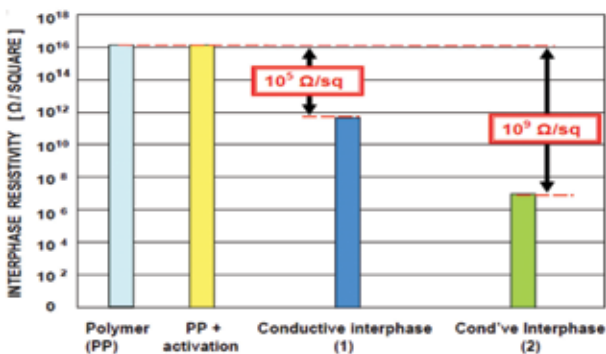


Fig. 9. Surface resistivity of an automotive polypropylene blend (Polypacific Corton PDR 1024/5; HDT = 115°C): untreated; flame-treated and surface-modified by electro-conductive adhesion promoting molecules

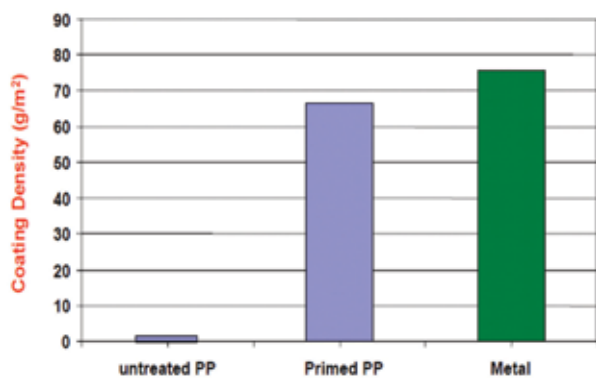


Fig. 10. The effectiveness of powder transfer to the surface of automotive polypropylene blends (Polypacific Corton PDR 1024/5; HDT=115°C) surface-modified by electro-conductive adhesion promoting molecules (No 1 in Figure 9) in comparison with an untreated PP and metal (steel) substrate

4. Robotic treatment and powder coating of full-size PP-based engine block covers

Full scale industrial trials of powder coating polypropylene on V8 engine block covers depicted in Figure 11 were conducted at Coating Services Australia, CSA (Dandenong, Vic). The mouldings were first surface treated using a CSIRO Pilot Plant robotic facility illustrated in Figure 11 in a sequence comprising: (1) flame activation, and (2) conductive primer spray.

Approximately 20 surface-modified mouldings were then suspended on the conveyer line in the industrial powder-coating facility of Coating Services Australia (CSA), powder coated, and then cured in the tunnel baking oven. Photos in Figure 12 provide comprehensive illustrations of all stages of the industrial scale powder coating process. The quality of the surface of the powder coated mouldings was excellent, with no surface defects detectable on any of the mouldings submitted for the above trials.

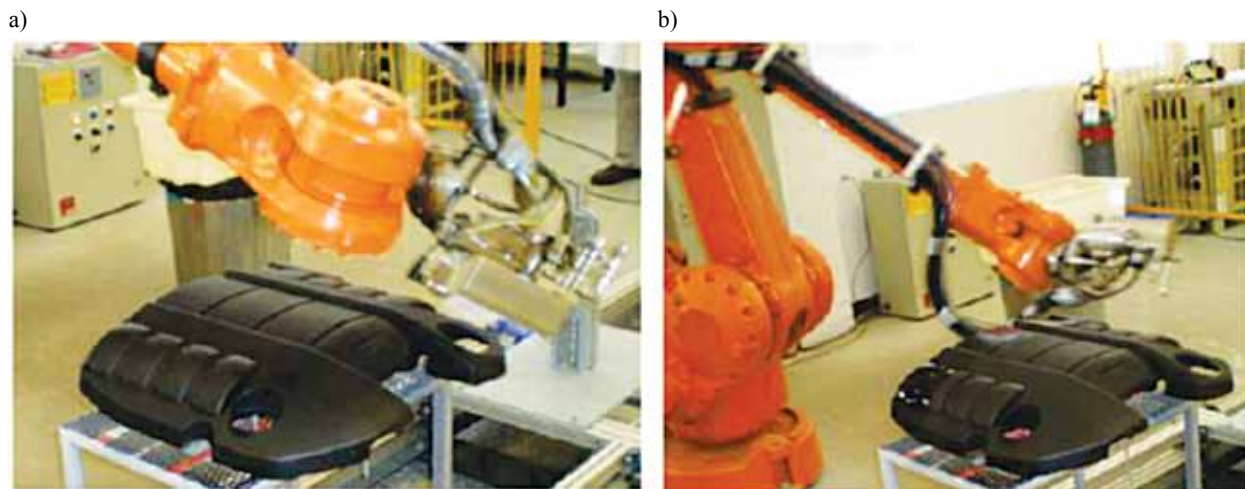


Fig. 11. Surface treatment of polypropylene mouldings of V8 engine block covers using fully automated robotic facility: a) flame activation, and b) conductive primer spray

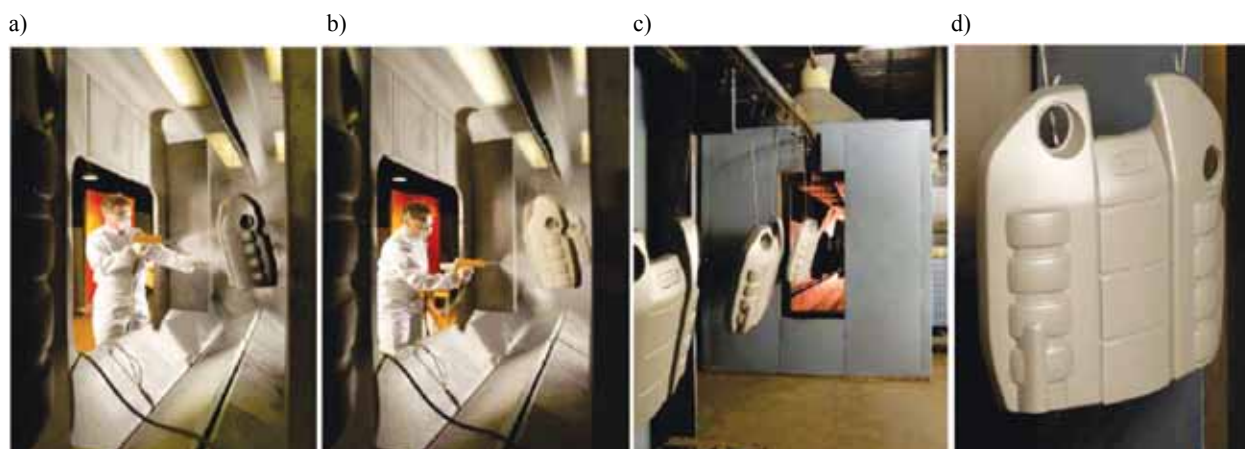


Fig. 12. The full sequence of industrial scale powder coating of surface-treated polypropylene mouldings of V8 engine block covers at the CAS production facility: (a) 1st stage of powder coating depicting a partially coated moulding; (b) completely powder coated component; (c) powder coated mouldings at the exit from the baking oven; (d) finished product: powder coated V8 engine block cover with fully cured coating

5. Performance assessment of powder coated plastics

Four (4) full-size polypropylene engine block covers (V8 engine) were surface treated by CSIRO and powder coated with Dulux Powder Coating Customcoat QP Engine Silver.

The samples were submitted to the Amdel Materials Services Laboratory for full evaluation testing in accordance with HN 2184: 1999. All tests were completed in triplicate excluding the “Moisture & Cold cycle” and “Temperature resistance” tests which were carried out on the entire engine cover. Table 1 provides a comprehensive summary of the tests outcome.

Table 1. The outcome of independent testing in compliance with: (1) HN2184, 1999, and (2) requirements of statistical analysis of test data and reporting

HN 2184 Clause	Test	Exposure Specification	Minimum requirement	Result (average)
3.1	Adhesion (Cross-Hatch)	Initial adhesion	rating 8	9.8
		Humidity exposure (72 hrs)		8.0
		Water immersion (2 hrs)		8.0
3.2	Brittleness	Scribe through coating	no cracking	P/F/P

HN 2184 Clause	Test	Exposure Specification	Minimum requirement	Result (average)
3.3	Moisture & Cold Cycle (15 cycles)	20 hrs at 38°C/100% RH	no cracking	Pass
		3 hrs at -18°C		
		1 hr at RT		
3.4	Resistance to Oil (Cross-hatch adhesion)	7 hrs immersion in oil at 68–74°C	no cracking	Pass
3.5	Resistance to Petrol	30 rubs (unleaded petrol)	<ul style="list-style-type: none"> • no cracking • no swelling • no blisters • gloss stability 	Pass
		10 cycles petrol immersion		Pass
3.6	Temperature Resistance (Cross-hatch adhesion)	168 hrs at 140°C	rating 8	10
3.7	Resistance to Gasohol	30 rubs (unleaded petrol)	as Clause 3.5	Pass

Conclusions

1. Surface resistivity of CSIRO-treated polymer surfaces achieves 10^{-6} to 10^{-8} Ω /square, which is 3 to 5 orders of magnitude below the electrostatic coating applicability threshold of 10^{-11} Ω /square.
2. New powder coating resins (Dulux Powder Coatings) are capable of curing at temperatures of 130–135°C, which is significantly below the thermal deflection temperature of typical PP-based automotive polyolefin blends.
3. The outcome of industrial trials carried out in commercial facility of Coating Services Australia/Dandenong (CSA) with the use of full size automotive components (PP-based engine block covers) fully demonstrated the suitability of the developed technology for prospective industrial applications targeting the substitution of the current liquid paints by low-temperature cured zero-waste powder coatings.

References

1. Gutowski W.S., Li S., Russell L., Filippou C., Hoobin P., Petinakis S.: Theoretical and Technological Aspects of Surface-Engineered Interface-Interphase Systems for Adhesion Enhancement. *Journal of Adhesion*, 2003, 79, pp. 483–519.
2. Gutowski W., Wu D.Y., Li S.: *Surface Treatment of Polymers*. US Patent No. 5,879,757, 1999.
3. Wu D.Y., Li S., Gutowski W.S.: *Surface Treatment of Polymers*. US Patent No. 5,922,161, 1999.
4. Gutowski W., Wu D.Y., Li S.: *Surface Treatment of Polymers*. Australian Patent No. 680716, 1998.
5. Toikka G., Liu M.S., Gutowski W.S., Gengenbach T.: *Molecular interactions between protonated polyethylene-imine and mica*. CSIRO Report (3-F-2013).