MULTIFUNCTIONAL INTERPHASES FOR POLYMERIC ENGINEERING PRODUCTS AND SMART DEVICES

Voytek S. Gutowski, Gary Toikka, Ming S. Liu, Sheng Li

S u m m a r y

The ability to control interactions between polymeric substrate and single molecules including successful placement of molecules in desired location at technologically useful conformation and spatial architecture provides a platform for designing functional surfaces for high-tech engineered products and smart devices. Subsequent ability to control interactions between arrays of immobilized molecules in the form of molecular brushes and interacting materials such as fluids, solids or bio-active materials such as cells and tissues facilitates the control of adhesion and fracture properties of interfaces for structurally bonded or coated materials or enables control of other properties such as surface conductivity of flexible films, fibres and fabrics for electronic or energy harvesting applications, live cells propagation in bio-medical sensors or devices and for restorative medicine applications. This paper discusses theoretical and practical aspects of surface grafted molecular brushes at controlled surface density, spatial geometry and chemical functionality which facilitate more than 1000-fold strength increase of bonded assemblies in comparison with unmodified substrates to the point of achieving 100% cohesive fracture of substrates or adhesives, as detailed in our earlier publications. The same molecules exhibiting an in-built electron conductivity facilitate achieving a 10^8-fold increase in polymer surface conductivity.

Keywords: polymers, polyethyleneimines, aminosilanes, protonation, surface conductivity, electrostatic deposition, adhesion, coatings

Wielofunkcyjne warstwy dla polimerowych wyrobów i urządzeń inteligentnych

S t r e s z c z e n i e

Analiza oddziaływania podłoża polimerowego i pojedynczych cząsteczek dotyczy ich rozmieszczenia dla ustalonego położenia w celu uzyskania korzystnej technologicznie konfiguracji. Stanowi ona podstawę do projektowania struktury geometrycznej powierzchni zaawansowanych technologicznie wyrobów i urządzeń inteligentnych. Określenie stopnia wzajemnego oddziaływania pomiędzy układami cząsteczek w postaci „szczotek molekularnych" – substancjami w stanie ciekłym i stałym lub materiałami bioaktywnymi, m.in. komórkami i tkankami, umożliwia kontrolę przylegania i pękania materiałów połączonych. Także kontrolę innych właściwości m.in. przewodnictwa powierzchniowego wytworzonych warstw lub włókien oraz rozprzestrzeniania się komórek w czujnikach i urządzeniach biomedycznych. W pracy przedstawiono teoretyczne i praktyczne zagadnienia z obszaru „szczotek molekularnych". Uwzględniono kontrolę ich gęstości powierzchniowej, geometrii i właściwości chemicznych. Umożliwi to zwiększenie wytrzymałości łącznych elementów ponad 1000-krotnie w porównaniu z podłożem niemodyfikowanym. Zapewni także pękanie kohezyjne podłoża lub warstwy klejów.

Słowa kluczowe: polimery, przewodnictwo powierzchniowe, osadzanie elektrostatyczne, powłoki adhezje

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1. Introduction

Smart materials with ability to respond to external stimuli such as electric current, light, or magnetic field are required for functioning and control of related smart devices. This, in turn, stimulates rapid growth of demand for polymers exhibiting multifunctional bulk or surface properties or features which are mandatory for fabrication of passive-, or active-control devices in a broad range of high-tech applications such as optoelectronics, biomedical devices, sensors, packaging, textiles, aerospace, energy storage and conversion, security and military applications. Examples of practical applications are: adhesion enhancement combined with the "dismantle-on demand" capability, photo-chromic effects including controlled colour and surface patterns on switchable see-through or screening panels or camouflage materials, transparency and surface conductivity and good multi-layered materials adhesion on large-area "roll-up" display screens, electroluminescent lighting or energy conversion panels, etc.

Live cells and tissues are also known to be responsive to electrical field and signals and hence, electroconductive polymer surfaces would provide a feasible platform for a number of biological and medical applications of polymers in areas such as biosensors, live cells proliferation and fluid and tissue engineering including neural tissue regeneration.

Strong adhesion of adjacent materials such as adhesives or electro-fluorescent coatings in light emitting devices to a polymeric substrate, or that of reinforcing fibres to composite matrix or that of a stem of hip implant to human femora are other types of essential requirements in designated industrial or biomedical applications.

One of the key objectives of research in this rapidly growing field of science and technology is integration of different types of functionalities through controlling the functionality and structure of interphases at the molecular level. The key challenge stems from the requirement for the control of a number of surface functionalities or properties simultaneously. This includes: (i) excellent adhesion between polymeric substrate (often, a thin film) and the functional coating, (ii) adhesion enhancement combined with the "dismantle-on-demand" capability, (iii) high surface conductivity and controlled charge character, mobility and density, (iv) high optical clarity, (v) controlled opto-electronic and/or opto-chromic properties, and other.

The above properties can be feasibly achieved through designing engineered interphases comprising arrays of surface grafted functional mo-lecules exhibiting designated features such as surface chemistry, 2-D and 3-D interface architecture, adhesion control features, opto-electrical and other surface properties which, in turn, control designated multifunctional properties of a polymer and based on it smart engineering system or device.

We demonstrate in this paper that significant enhancement of substrate performance can be achieved in such applications through the use of appropriately selected and distributed connector molecules which are grafted to surfaces of substrates at distribution and properties profile ascertaining a range of desired surface functionalities. Understanding of mechanisms of a wide array of physico-chemical and mechanical aspects of interactions between connector molecules and bonded materials provides tools for designing interfaces and interphases and subsequently fabricating substrates exhibiting an array of functionalities essential for appropriate functioning of end-products such as:

- an aerospace composite structure with significantly improved strength and durability,
- electro-conductive and adhesion promoting flexible film for printable lighting panel or solar cell,
- electro-conductive and adhesion promoting surfaces of automotive plastic products for electrostatic deposition of zero-waste powder coatings and wet paints, or
- electro-conductive bio-scaffolds for propagating controlled growth, under conditions identical to the *in-vivo* environment, of skin tissue or nerve cells and structures for regenerative medicine and other life- and health-saving surgical implants.

2. Interactions of single molecules of multifunctional graft chemical with the substrate

This work focuses on systems providing combination of surface conductivity, adhesion promotion and bio-compatibility through the use of selected molecules containing simple aliphatic amine groups such as polyethelene imines (PEI) and amino-silanes (Fig. 1). When grafted to polymers preoxidized by corona discharge, plasma, UV radiation or flame treatment, these categories of molecules facilitate control of surface architecture at polymer interfaces, and convert their chemically inert, non-conductive surface into good surface conductors whilst simultaneously providing excellent adhesion of coatings, adhesives, printing inks and biomaterials, including live cells proliferation [1-4]. Oxygenated species, e.g. COOH or OH created by mild surface oxidation form a dense 2-dimensional array of reactive sites providing a scaffold for subsequent attachment of linear or branched polyethylene imines (PEI) and other polyamines, or amino-silane molecules through their functional groups bonding through either hydrogen, ionic or covalent bonds, as illustrated in Fig 2.
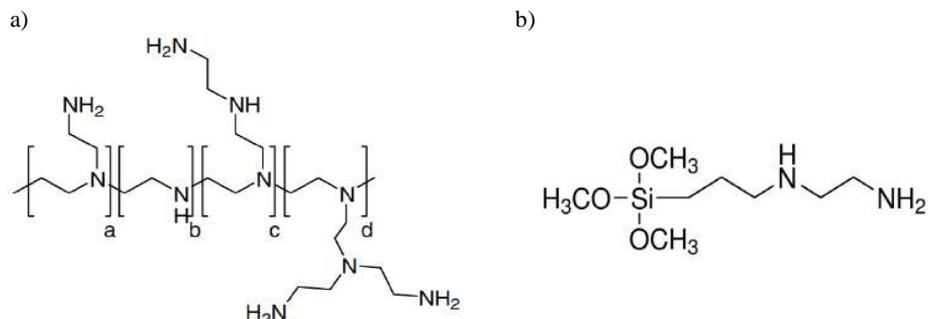
a)   b)

Fig. 1. Chemical structure of graft molecules Polethyleneimine (PEI) (a)
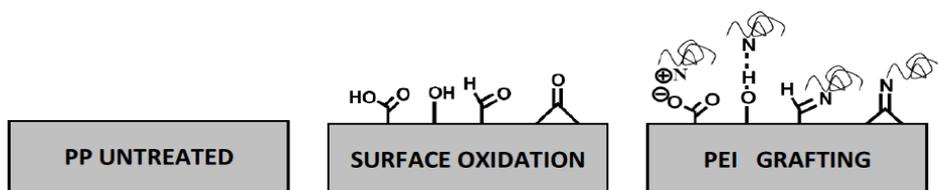and N-(2 aminoethyl)-3-aminopropyl-trimethoxysilane: Z-6020 (Dow Corning) (b)

Fig. 2. Schematics of surface grafting PEI molecules onto surface-oxidized polymers, e.g.,
polyolefins

To elucidate the mechanisms of interactions of individual molecules of cationic PEI with the surface of negatively charged COOH sites, an atomically smooth Muscovite mica was used as an analogue substrate model. This facilitated simulation of interactions of PEI molecules with oxidized surface of polymers such as PP or PE including elucidation of the mechanisms of spatial architecture control of resultant interphases by modeling programs utilising molecular and quantum mechanics in DMol3 environment (Materials Studio, Accelrys). Figure 3 illustrates selected consecutive stages of adsorption of PEI macromolecues onto the surface of negatively charged model substrate from water-based carrier solutions at a neutral charge (pH $\approx$ 10.3 / unprotonated state) or as 75% protonated molecules (solution at 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 increased aspect ratio of adsorbed molecules, i.e.: (i) an increased footprint of docked molecules, (ii) increased height of the vertically stretched strands, and (iii) increased, i.e. almost doubled number of hydrogen bonds in protonated PEI resulting from increased electrostatic interaction bringing the molecular groups into closer contact with the substrate surface. Conformational gains illustrated in Fig. 3 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.
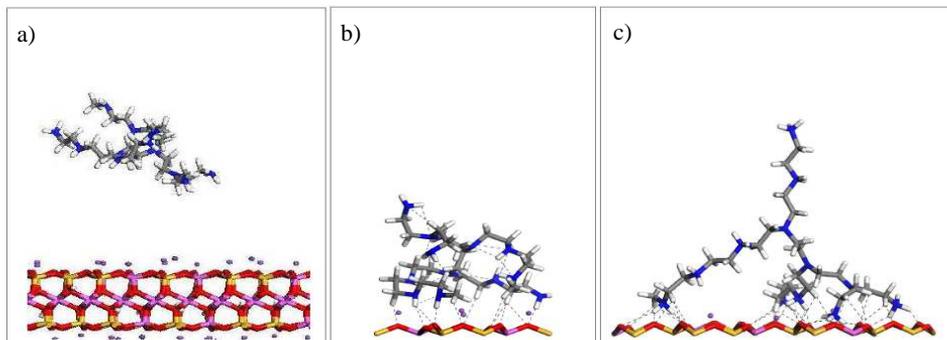
Fig. 3. Adsorption and surface conformation of PEI macromolecules, unprotonated (pH10.3) and highly protonated (75%, at pH6.0), on the surface of negatively charged model substrate: a) initial condition, in aqueous environment, b) unprotonated PEI molecule, c) highly protonated, adsorbed, PEI molecule [5]

Such interphase-interface system fabricated on the polymeric substrate surface (see Figs. 3 and 5a), provided by an array of surface grafted connector molecules, forms an intermediate zone between the functional substrate and the adjacent material such as adhesive, coating or biological cells or tissues and is subsequently able to interact with such materials through interpenetration (reptation), or van der Waals interactions, or chemical bonding.

3. Adhesion control by surface grafted molecular brushes

3.1. Adhesion enhancement through connector molecules chemically bonding with adhesive

Adhesion and fracture performance of interfaces between a polymer and adhesive or coating are significantly improved by surface-grafted connector molecules which act through either, or the combination of: (i) chemical reaction/crosslinking with the adjacent material e.g. adhesive, and/or (ii) interpenetration into such material.

Theoretical principles of adhesion enhancement by connector molecules were developed by de Gennes [6, 7]. He elucidated the mechanisms of adhesion control by a load-bearing interface comprising an array of surface grafted macromolecules (Fig. 4) interacting through the following alternative mechanisms: (i) chain pull-out, (ii) chain scission, and (iii) craze formation (in ductile polymers) ahead of the propagating crack tip.

The interphase-interface system, which is an intermediate zone between the polymeric substrate and adhesive or coating (see Fig. 5a) may be decorated with an array of surface grafted connector molecules interpenetrating into or chemically bonding with an adhesive. If both ends of graft molecules are

chemically bonded to the substrate and adhesive, or are sufficiently long to be well "anchored" in the bulk volume of an adhesive through entanglements, the interface will fail through multiple chains scission. An array of molecules crossing the interface at surface density σ increases load-bearing capability of interface to the level of breaking stress, $\sigma T \sim Fb\,\sigma$, where Fb is the force required to break individual molecular chains (approx. strength of C-C bond = = 1 mN).

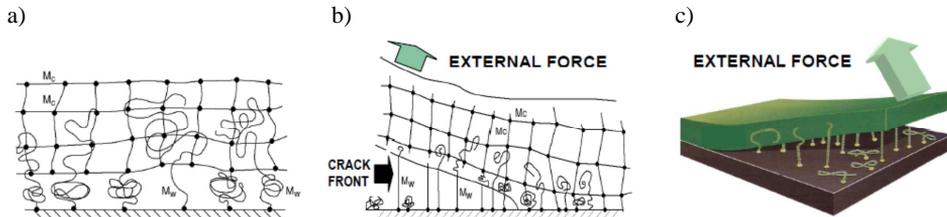a)   b)   c)

Fig. 4. Schematic performance of adhesion enhancing interphase comprising surface grafted molecular brush on adhesively bonded or coated polymer: a) initial stage before external force application; M_w – molecular weight of surface grafted molecules, M_c – molecular weight of chains between cross-links of crosslinked adhesive or paint, b) interfacial crack propagation, c) 3-D visualization of interpenetrated connector chains pull-out from the body of an adhesive not reactive with connector molecules (interacting solely through van der Waals interactions)

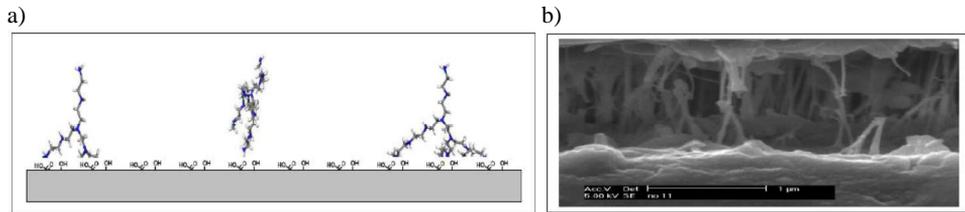a)   b)

Fig. 5. Schematics of an interphase/interface system decorated with molecular brush fabricated through chemical grafting of molecular chains of PEI to pre-oxidized (corona-discharge) surface of a LDPE (low density polyethylene) substrate for adhesive bonding with chemically bonding cyanoacrylate adhesive (a) and Scanning Electron Microscope (SEM) (b) photo of fractured bondline cross-section of assembly comprising 2 pieces of LDPE surface grafted with PEI molecules (see 5a) and subsequently bonded with cyanoacrylate adhesive (Loctite 406)

According to Raphaël [8] theory, adhesion enhancement (fracture energy) by surface-grafted chains is:

$$G_b = W_a + W_b\,N{\cdot}\sigma \qquad\qquad (1)$$

where N is the degree of polymerisation of connector molecules, W_a is reversible energy of adhesion between the bare (ungrafted substrate) and the adjacent

polymer (due to van der Waals forces only), and W_b is the energy required to disrupt a dense array of chemical bonds as given by the following: $W_b = U_b / a^2$, where U_b is the energy of a bond occupying an area of a^2.

3.2. Adhesion enhancement through connector molecules interpenetrating into adhesive

The overall effectiveness of an array of interpenetrating connector molecules (Fig. 4-6) depends on their surface density, the length of individual molecules and optimum surface density in relation to their length [9, 10].
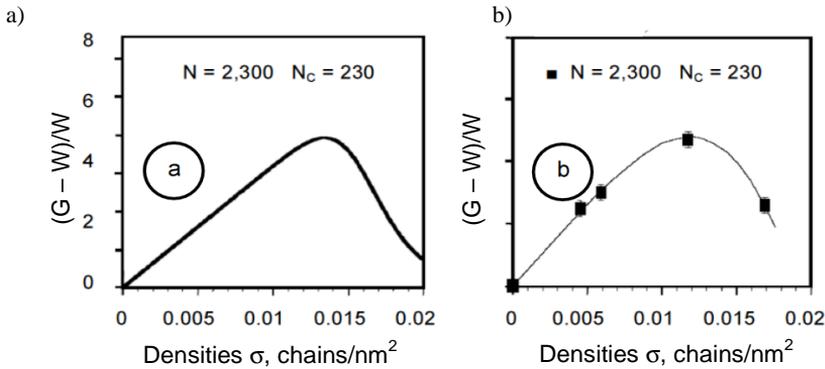

Fig. 6. Adhesion between silicon wafer and PDMS elastomer in relation to surface density of surface grafted PDMS connector molecules: a) theoretical value of normalised fracture energy $(G - W)/W$ estimated through the use of Eqn (2) for connector molecules characterized by $N = 2300$ interacting with crosslinked PDMS elastomer exhibiting $N_c = 230$ [11], b) experimental data obtained for chain densities of: 0,005; 0.006; 0.012 and 0.017 chains/nm^2

According to de Gennes [6], for the interface reinforcement involving chain pull-out in the presence of van der Waals interactions only (when connector chains and adhesive's polymer are identical) the fracture energy, G, associated with deformation and extraction of unbonded chains is:

$$G = 2\gamma(1 + \sigma N) \tag{2}$$

where γ is surface energy of the polymer and connector chains' and σ is the surface density of connector chains.

De Gennes demonstrated that the normalised increase in fracture energy of interfaces "decorated" with grafted connector molecule chemically identical with an elastomeric adhesive is as follows [11]:

$$G - W \cong \gamma N\sigma(1 - \sigma^{2/3} N_c^{1/3}) \tag{3}$$

where: W is the energy of adhesion ($W = 2\gamma$) between the chemically identical PDMS adhesive and PDMS connector molecules; N is degree of polymerisation ($N = M$W/m) of connector chain molecules, and N_c is degree of polymerisation of crosslinks of the PDMS adhesive.

Figure 6a presents graphical form of Eqn (3) numerically solved for N = 2,300, N_c = 230, and γ = 21.6 mJ/m^2 at 25°C [11]. The results confirm a distinct optimum (σ_{OPT}) in the surface density (σ) of the connector molecules which has to be achieved, as predicted by see Eqn 3, in order to maximize forces of adhesion between a surface-modified substrate and adhesive. Experimental data (Fig. 6b), demonstrate excellent agreement with theory.

4. Experimental

4.1. Surface grafted connector molecules for adhesion enhancement

The effectiveness of adhesion enhancement by surface grafted PEI molecules interpenetrating into adhesive was investigated using the following materials: (i) *substrate*: PP – untreated and surface treated with corona discharge; (ii) *adhesive*: pressure-sensitive acrylic PSA tape VHB 4959/3M; (iii) *connector molecules*: PEI/BASF (pH10.3): MW = 800 (N = 19) / MW = 1300 (N = 46) / MW=25,000 (N = 581) / MW = 750,000 (N = 17,442) in water: at 10^{-5}; 10^{-4}; 10^{-3}; 10^{-2}; 0.1; 0.5 and 2%. *Adhesion strength*: by 180º peel test [12] using conditioned specimens: (i) 2 days/20°C, and (ii) 12 hours/60°C: to promote molecular brush reptation into the adhesive layer.

Figure 7 clearly demonstrates that for all lengths of surface grafted PEI connector chains (N = 19 to 17,440) a distinct optimum of surface density (σ_{OPT}) of graft molecules is observed at which the maximum strength of adhesion is achieved. This constitutes good agreement with Eqn (3). It is also seen in Fig. 7 that the maximum reinforcement of interface occurs at the chain length of N = 580.

All interactions present in the experiments illustrated in Fig. 7 are of the van der Waals type only, with the peel strength, and corresponding fracture energy increase resulting purely from the disentanglement and molecular chains extraction from the crosslinked matrix of pressure-sensitive adhesive used in our experiments.

4.2. Multi-functional application: surface conductivity and adhesion enhancement

As illustrated in Fig. 8, 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 Fig. 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 neighboring PEI molecules, as illustrated in Fig. 3.
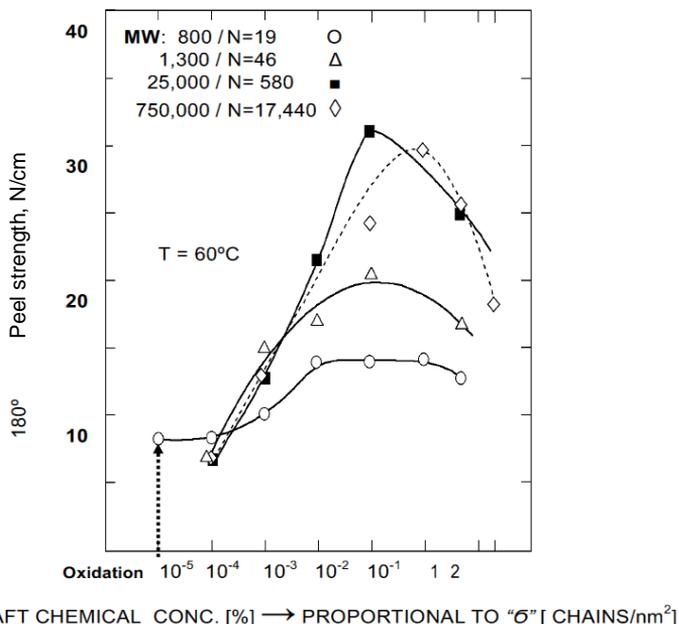
Fig. 7. The influence of surface density and length of graft chemical molecules (related to N = degree of polimerisation) on adhesion enhancement between polypropylene substrate decorated with surface grafted PEI macromolecules of varying length (N = 800 to 17,440), interacting with chemically non-reactive pressure-sensitive acrylic adhesive (PSA tape VHB 4959/3M)
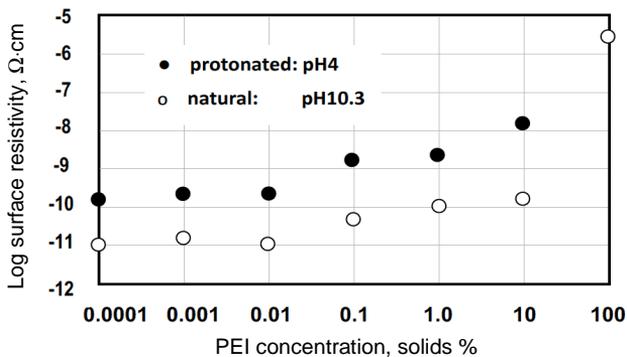
Fig. 8. Surface conductivity of thin films of PEI (MW 800) on Muscovite mica

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

Owing to permanent attachment of individual PEI molecules in the form of highly ordered surface structures (Fig. 3c and 5), 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 application of low concentration water-based PEI solution, 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} $\Omega \cdot cm$ into highly surface-conductive materials exhibiting long-term stable surface resistivity at the level of 10^{-8}-10^{-7} $\Omega \cdot cm$. This constitutes an approximately 8 orders of magnitude increase in surface conductivity due to creation of conduit for electron transfer across a dense surface array of protonated amine groups of PEI.

Low surface resistivity (10^{-8}-10^{-7} $\Omega \cdot cm$) 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 Fig. 9. Such electrostatically assisted transfer of coating particles drastically improves the coating's transfer effectiveness in comparison with unassisted applications; from approximately 40 to 60% in wet painting, and reaching approximately 95-98% in powder coating. Such effectiveness of surface finishing or coating processes is not available whilst using the current generation (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 elimination of need for water curtain catching wet paints overspray in commodity painting processes.
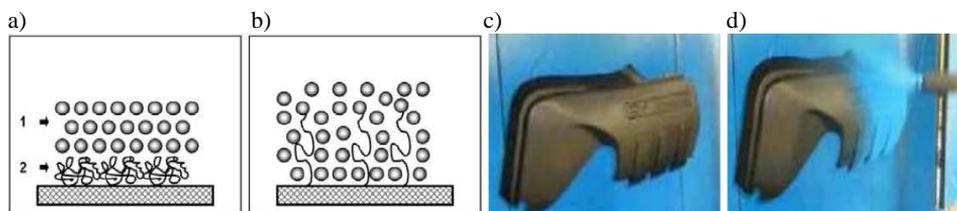

Fig. 9. Schematics of polymer surface modification by protonated PEI molecular brush for surface conductivity and adhesion enhancement: a) electro-conductive surface state with collapsed (coiled) PEI molecules, b) adhesion-promoting surface state: PEI molecules unfold upon heat impulse (during thermal cure of powder coating) or on contact with wet paint (in wet-spray painting), subsequently penetrating into a layer of wet paint or powder particles, c) PP-based engine block cover (GM 4-cylinder engine) with PEI electro-conductive nanocoating, and d) powder coating effectiveness: an excellent electrostatic transfer of powder particles (20 μm) onto the surface-
-conducting polymeric product

The process illustrated in Fig. 9 is industrially trialed in surface finishing and assembly processes utilizing polymeric and composite-based products for a range of automotive, construction and appliances applications requiring surface finish suitable for exterior applications associated with the need for high-durability, high scratch resistant coatings.

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