

THEORETICAL AND TECHNOLOGICAL ASPECTS OF SURFACE ENGINEERING FOR ADHESION ENHANCEMENT OF POLYMERS AND COMPOSITES

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Abstract

Polymers and lightweight composites rapidly replace metals in high-tech engineering applications in automotive, aerospace, shipbuilding, civil and other engineering applications. Due to chemical inertness, hydrophobicity, surface contamination and migrating functional and processing additives, most polymers require surface modification to ascertain high strength and reliability of bonded products. In structural bonding, the key objective is creation of permanent bond between bonded elements. The overarching aim is creating such strong adhesion forces between bonded material and adhesive that the bond becomes unbreakable and the adhesive or substrate become the weakest element of the structure, thus enabling application of verifiable engineering design principles ascertaining reliable performance of structures throughout entire service life under the influence of all static, dynamic and environmental loads and impacts. Theoretical and engineering aspects of the problem, including criteria for attaining such bond properties, including experimental data, are comprehensively discussed in this paper. Examples of industrial applications of the technology are provided.

Keywords: Polymers, composites, thermoplastic olefins (TPOs), surface modification, molecular brushes, adhesion, adhesive bonding, coating

Teoretyczne i technologiczne aspekty połączeń materiałów polimerowych i ich kompozytów oraz kryteria ich oceny

Streszczenie

W wielu gałęziach techniki, m.in. lotnictwie, okrętownictwie i budownictwie, zwiększa się ciągle zastosowanie polimerów i kompozytów lekkich. Wykonanie z polimerów wyrobów złożonych często wymaga klejenia. Polimery są zwykle obojętne chemicznie, natomiast elementy wykonane z polimerów mają zanieczyszczoną powierzchnię i zawierają różne mikrodotadki. Stąd niezbędna jest modyfikacja ich powierzchni w celu zapewnienia odpowiedniej wytrzymałości łączonych elementów. Podstawowym zagadnieniem jest zapewnienie trwałego połączenia pomiędzy składowymi elementami. Konieczne jest wytworzenie określonej siły adhezji pomiędzy warstwami kleju i materiałem – polimerami. Dla zapewnienia nierozrywalności połączenia przyjmuje się, że klej lub materiał stanowią najsłabsze elementy konstrukcji. Umożliwi to zachowanie odpowiednich właściwości użytkowych klejonych elementów w warunkach oddziaływania obciążeń statycznych i dynamicznych. W pracy przedstawiono rozważania teoretyczne i praktyczne dotyczące tego zagadnienia. Przedstawiono kryteria oceny wytworzonych połączeń, dane doświadczalne oraz przykłady ich zastosowania w przemyśle.

Słowa kluczowe: polimery, kompozyty, olefiny termoplastyczne, modyfikacja powierzchni, wiązania adhezyjne, powłoki

1. Introduction

Manufacturers of commercial and military aircraft are vitally interested in maximising the contents of carbon- and glass-fiber reinforced thermoplastic composites in the manufacture and assembly of large primary structures such as tail, wing and fuselage offering substantial weight reduction, up to 50%, in comparison with aluminium components. The key candidate thermoplastic polymers considered in such applications are polyetheretherketone (PEEK), polyetherketoneketone (PEKK), polyetherimide (PEI), polyphenylene sulfide (PPS) and other high-tech engineering plastics. In the automotive industry, the weight reduction and associated fuel consumption economy are also the key drivers in increasing contents of polymeric blends and composites in car bodies. The key polymers of interest here are polyolefins, predominantly polypropylene, which finds wide use in the manufacture of bumper bars, interior body trim panels, instrument panel and wide range of other exterior and interior components. High-strength thermoplastic polymers and composites based on nylon, polyacetal and polycarbonate also find increasingly broad use.

It is demonstrated in this paper that significant adhesion enhancement in bonding and coating polymers and composites can be achieved through the use of specific connector molecules chemically attached (grafted) to the molecular backbone of a polymeric substrate. The effectiveness of interface reinforcement is shown to depend on: surface density of grafted molecules; length of individual molecules, and optimum surface density of connector molecules. The optimum conditions for adhesion enhancement are specified and verified by experimental examples. Examples of a relatively simple and industry-feasible technology for surface grafting connector molecules for enhancing adhesion of automotive TPO's are also discussed in detail.

2. Polymer- polymer interface reinforcement by surface grafted molecular connector chains

2.1. Modes of Molecular Connectivity Between Bonded Polymers

The bond strength and structural performance of adhesively bonded assemblies comprising polymers or composites is controlled by physico-chemical structure and properties and spatial architecture of interphase, an intermediate zone between the substrate and adhesive schematically illustrated in Fig. 1. It comprises an array of "connector chains" which, at one end, are chemically attached (grafted) to the molecular backbone of a polymeric substrate whilst the unbonded "free end" (see Fig. 1a), on application of chemically crosslinking adhesive becomes chemically bonded to it (see Fig. 1b), or alternatively on contact with a molten thermoplastic or soft elastomeric polymer

interpenetrates into the bulk of this material (Fig. 3c) providing adhesion enhancement.

The mechanisms of alternative interfacial interactions between the surface of polymeric solids onto which flexible molecular chains have been end-grafted, and another polymeric material such as adhesive, through either chemical bonding or molecular chain interpenetration have been explored by numerous researchers [1-21] who determined that the following mechanisms, schematically illustrated in Fig. 2, may contribute to the fracture of such interface reinforced by “flexible connector chains”: (i) chain scission, (ii) chain pull-out, and (iii) craze formation (in ductile polymers).

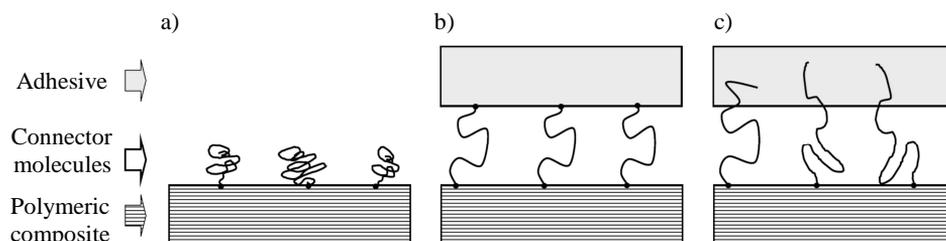


Fig. 1. Schematics of molecular brush interphase between polymeric substrate and adhesive, and that of the connectivity mode: a) prior to bonding: substrate surface decorated with chemically grafted flexible molecular chains (connector molecules), b) connector molecules unfolded and chemically bonded with adjacent adhesive, c) connector molecules interpenetrated into adhesive layer

Increasing the load-bearing capability of the interface (Fig. 1) relies on inserting, to a desirable optimum, molecular bridges connecting a substrate with adhesive, paint or other material, and the mode of molecular bridge connectivity between these materials.

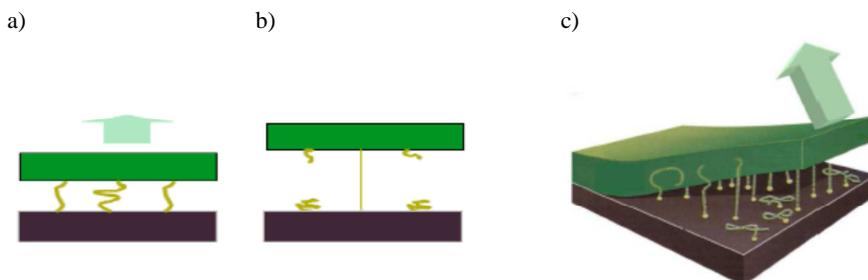


Fig. 2. Interfacial failure mode for two principal connectivity modes of surface grafted flexible molecular chains: a) substrate-adhesive assembly chemically bonded by an array of molecular bridges before strain application, b) chain scission along the interface upon excessive deformation causing rupture of single C-C bonds, c) surface grafted connector molecules interpenetrated into adhesive layer are gradually extracted from elastomeric adhesive along propagating crack front

If the both ends of connector molecules are chemically bonded; one end to the substrate and the other to an adhesive (Fig. 2a) whilst surface density, σ , of molecular chains bridging the interface is below the minimum required for exerting stress level causing yielding of one of adhering polymers (Fig. 2b), then on exceeding the failure stress, individual C-C bonds are broken (*at forces of approx. 1 mN*) along the backbone of individual connector chains.

Under conditions as above, interfacial delamination occurs along an interface subsequent to molecular chains scission at the stress, S_i , which is:

$$S_i \sim f_b \sigma \quad (1)$$

where f_b is the force required to break individual chain, and σ , surface density of grafted chains.

2.2. Surface Grafted Connector Chains Chemically Bonded with Adhesive

Theoretical aspects of adhesion enhancement of solid surfaces by grafted connector chains chemically bonded with polymers (see Fig. 2a and 2b) were explored by Brochard-Wyart and de Gennes [18] whose overall work in this area provided foundations of this field of science.

Adhesion forces between chemically inert, smooth solid surface and most adhesives are typically attributed to weak van der Waals interactions. Under external load such systems typically fail through interfacial fracture occurring as a delamination along a sharp substrate-adhesive interface.

Conversely, end-grafted molecular chains at surface density σ (sufficiently low so that each chain acts independently increase the load-bearing capacity of the interface linearly with increasing graft surface density, as per Eqn. (1) whilst bond energy, G_b , of such ‘‘chain-bonded’’ interface becomes:

$$G_b = W_a + W_b N \sigma \quad (2)$$

where: W_a is a reversible energy of adhesion between the bare (ungrafted) substrate and the adjacent polymer (van der Waals forces only), σ is the chains surface density, N is the degree of polymerisation of connector molecules, and W_b describes the energy required to disrupt a dense array of chemical bonds as given by the following:

$$W_b = \frac{U_b}{a^2} \quad (3)$$

where U_b is the energy of a bond occupying an area of a^2 .

The key findings of Brochard-Wyart and de Gennes [18] are depicted in Fig. 3. These are: (a) an increase in surface density of grafted molecular chains results in a linear increase of the failure stress and interfacial fracture energy G_i , as per expression (1), (b) The linear increase of interfacial fracture energy (rupture of connector chains only) with increase in graft density occurs up to a certain cut-off value (σ_{CRIT}) provided by expression (4):

$$\sigma_{CRIT} = \frac{N_c^{1/2}}{N} \quad (4)$$

where N_c is the number of monomers between crosslinks of adhesive whilst N is the number of monomers per connector chain (degree of polymerisation of connector chain molecules), and (c) For graft densities higher than σ_{CRIT} no further increase in interfacial fracture energy (through chains scission) is expected; cohesive failure of a bonded polymer or adhesive is observed.

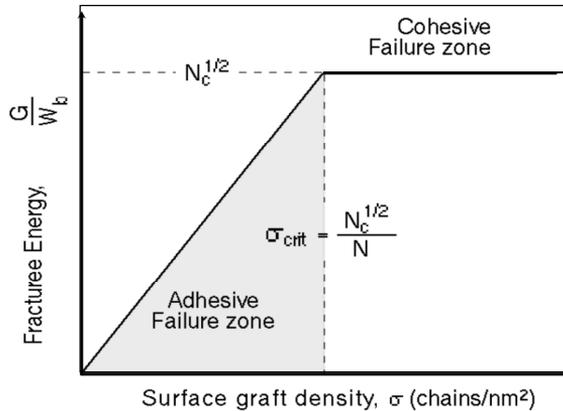


Fig. 3. Fracture energy and mode of interface fracture versus surface graft density, σ , in the case of grafted and chemically bonded macromolecular connector chains (based on [18])

2.3. Fracture of interfaces bonded through interpenetrating connector chains

The original concept of adhesion enhancement by connector molecules surface grafted to a substrate and interpenetrating into adjacent polymer was first proposed and discussed by de Gennes [1, 2]. The detailed mechanisms of complex physico-chemical interactions of surface grafted molecular chains with adjacent polymers were further elucidated by other researchers [3-13] who determined that fracture of connector-chain bonded interfaces can be attributed

to the following: (i) chain scission, (ii) chain pull-out, and (iii) craze formation ahead of the crack front.

According to de Gennes, in the simplest case of chains pull-out (Fig. 2c) in the presence of van der Waals interactions (when connector chains and adhesive polymer are chemically identical), the fracture energy associated with chains deformation and extraction is the connector chains is:

$$G = 2\gamma(1 + \sigma N) \quad (5)$$

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

De Gennes successfully demonstrated that the normalised increase in the fracture energy of such grafted interface, i.e. between solid substrate ‘decorated’ with PDMS (poly-dimethylsiloxane) flexible molecular chains, and the PDMS elastomeric adhesive is as follows [14],

$$G - W \cong \gamma N \sigma (1 - \sigma^{2/3} N_c^{1/3}) \quad (6)$$

where: G – fracture energy of the interface reinforced with surface grafted connector molecules; W – energy of adhesion ($W = 2\gamma$) between the chemically identical PDMS adhesive and PDMS chains; N – degree of polymerisation ($N = MW/m$) of connector chain molecules, and N_c – degree of polymerisation of crosslinks of the PDMS adhesive.

The following is seen from Eqn (2):

- i. For $\sigma > N_c^{-1/2}$ chains completely separate from the PDMS network and G reduces to W .
- ii. The optimum adhesion occurs for:

$$\sigma_{OPT} \cong 0.465 N_c^{-1/2} \quad (7)$$

- iii. The corresponding value of the optimum fracture energy, G_{OPT} , is:

$$G_{OPT} - W = 0.186 \gamma \frac{N}{N_c^{1/2}} \quad (8)$$

Solid black line in Fig. 4 illustrates the results of Eqn (2) solved numerically for $N = 2,300$ and $N_c = 230$, and $\gamma = 21.6 \text{ mJ/m}^2$ at 25°C [15]. The same authors experimentally verified the theoretical model described by Eqn (6). The surface density of PDMS chains grafted onto the surface of silicon wafer in their experiments was controlled by varying the PDMS concentration in graft carrier

solution. Experimental results in Fig. 4 (red squares and dotted line [17]) present the normalized fracture energy $(G - W)/W$ for the molecular brush/elastomeric adhesive interphase interacting through van der Waals forces only. It is apparent in Fig. 4 that good agreement between the theoretical predictions with experimental data has been achieved. The maximum adhesion energy occurs at graft molecules surface density of σ_{OPT} , which corresponds to the conditions under which total penetration of connector chains occurs. According to Vilmin *et. al* [16], the data in Fig. 4 yielded $\sigma_{OPT} = N^{1/10} / N_c^{-3/5}$. Although this differs from the original work of de Gennes ($\sigma_{OPT} \cong 0.465 N_c^{-1/2}$), a good qualitative agreement exists between both data sets.

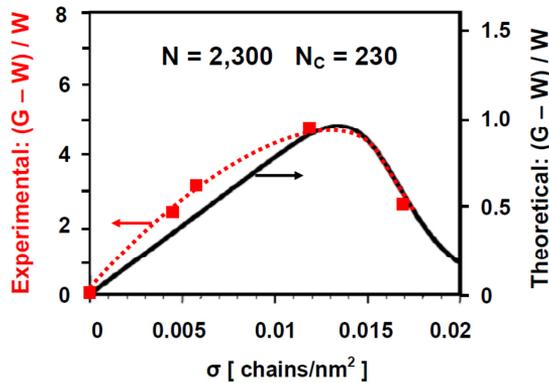


Fig. 4. Adhesion enhancement as a function of connector chains surface density (PDSM molecules: $N = 2300$) grafted onto silicon wafer. These were interacting (contact time: 15 h) with crosslinked PDMS elastomer, $N_c = 230$ [15]. W is thermodynamic work of adhesion, $W = 2\gamma(21.6 \text{ mJ/m}^2$ (based on [17]))

Overall, the collective work of a broad body of researchers [1-18] exploring adhesion enhancement by surface grafted connector molecules demonstrates that fracture performance of interfaces ‘decorated’ by surface grafted and interpenetrating connector chains is controlled by:

1. The length of connector molecules: determined by degree of polymerisation, $N = M_w/m$, where M_w is the molecular weight of the chain; and m : molecular mass of the monomer. The influence of connector molecule length is categorised as follows:

- short, unentangled, polymer chains ($N < N_e$): ($N_e \cong 200$ is the threshold of molecular entanglement) are too short to form entanglements with the adjacent polymer,

- entangled polymer chains ($N > N_e$): Long macromolecular chains ($N \geq 200$, can form physical entanglements with the adjacent, adhering polymer.

2. The surface density, σ [number of grafted molecular chains per nm^2].
3. The breaking strength, f_b , and fracture energy, G_c , of individual molecular chain: G_c/σ .
4. The formation (glassy polymers) of and subsequent failure of a craze ahead of the crack.

3. Experimental

3.1. Enhancement of adhesion by surface grafted molecular brushes

Untreated polymeric substrates such as PE, PP, PEEK, LCP, PPS and many other are not receptive regarding ability to chemically bind connector molecules through ionic or covalent bonding due to a lack of reactive chemical functionalities at their surface.

To facilitate surface grafting, polymer surface requires activation, e.g. through oxidation by flame, corona discharge, ozone, or UV treatment (see Fig. 5) which introduces receptor sites such as OH, C=O, COOH groups to the surface. These, in turn, form a dense surface array of reactive sites providing scaffold for grafting individual brush-forming molecules: polyethyleneimines (PEIs) or amino-silanes, as schematically illustrated in Fig 5c. The functionality of molecular brush-forming chains is chosen to provide chemical reactivity with an adhesive to be used for bonding a composite structural component, or to coat it with an appropriate decorative or functional coating.

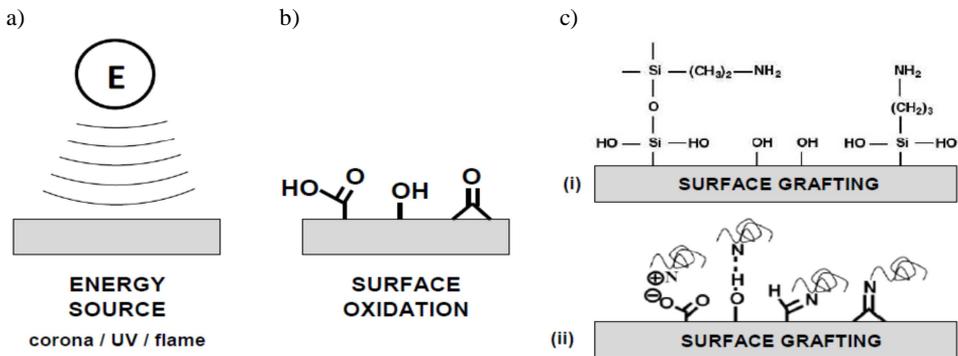


Fig. 5. Schematics of surface grafting process analysed in this paper: a) polymer surface oxidation by corona discharge, UV radiation, flame, oxygen plasma, b) typical surface chemistry of oxidised polyolefins, c) surface grafting: (i) amino-functional silane, and (ii) polyethyleneimine (PEI)

The process depicted in Fig. 5 provides the possibility of tailoring the surface chemistry of a polymer, without altering its bulk properties, in order to

optimise the adhesion between the surface engineered substrate and adhesive, or other materials.

3.2. Experimental

3.2.1. Methods, Equipment and Materials

Polymer pre-oxidation: was carried out by flame or corona discharge treatment, i.e.:

Corona discharge: Tantec EST HV 2010 unit (max. power output: 1 kW). Treatment speed: 0.1 to 70 m/min; electrode-substrate distance: 2.5 mm.

Flame treatment: Arcotec EFT 751 unit. Treatment conditions: (a) excess oxygen: 1.0%; treatment speed: 60 m/min; flame tip-substrate distance: 10-50 mm

Graft chemicals preparation and application

Organofunctional silane: N-(2 aminoethyl)-3-aminopropyltrimethoxy silane: Z-6020/Dow Corning

Silane was first hydrolysed (distilled water) at a 1:3 silane/water mole ratio for 24 h. The hydrolysed silane was then diluted with isopropanol to obtain a 0.05-1% range of concentrations. Oxidised substrates were immersed in silane solution. Alternatively spray application was carried out straight after corona or flame treatment followed by a moisture flash-off with an infra-red lamp.

Polyfunctional amines (PEI): MW = 800; 2000; 25,000; 750,000 (BASF). These were applied from water-based solution at the following concentrations: 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , 0.1, 0.5 and 2%.

Polymeric Substrates: EVA/PP blend, PP, HDPE

Silicone Adhesive: Silbion 70004/Rhone Poulenc

Elastomeric acrylic pressure-sensitive adhesive: VHB 4959 tape /3M

Test Methods

Shear Strength: was determined using single lap-shear specimens, 25 mm wide, with an overlap of 10 mm. All substrates were cleaned with isopropyl or ethyl alcohol prior to further treatment. Five replicates were tested in an Instron mechanical tester (10 mm/min) for shear strength [MPa].

Peel strength and fracture energy: was determined using 180° peel specimens (100 x 20 mm) prepared in accordance with ASTM C-794. The fracture energy was estimated by: $G_c = F_c (1 - \cos \alpha)/b$ (F_c is the peel force; b – specimen width, α – the peel angle). The top of peel specimens involving pressure-sensitive adhesive tape VHB 4959/3M was reinforced by 3M self-adhesive tape 3M 981 (reinforced with glass fiber strands) to prevent tape stretching.

XPS analysis (X-Ray Photoelectron Spectroscopy): XPS analyses were performed on a VG Escalab MkII spectrometer equipped with an Al K_{α} source, non-monochromatized (see [25] for all details).

3.3. Results and discussion

3.3.1. Spatial orientation of surface grafted amino-functional silane molecules

Amino-functional silanes such as N-APTMS are traditionally used as coupling agents for improving the strength and durability of adhesively bonded metals or glass fibre composites.

In these applications the primary mode of bonding the amino-functional silane is through the silanol-end of the molecule, as illustrated in Fig. 6b. The secondary mode of bonding is through hydrogen bonding between the silane's amino groups and either the silanol groups or hydroxyl groups present on the oxidized surface of glass or metal [22-25]. This mechanism, observed also in or LDPE grafting, is schematically illustrated in Fig. 6a. The main feature of Fig. 6 illustrates the XPS spectrum of the N 1s peak of N-APTMS surface-grafted onto LDPE substrate. The two components of the N 1s peak observed near 399.3 and 400.4 eV, are attributed to free and protonated amino groups, respectively. Based on the relative intensities of the two components, about 55% of the amino-silane was protonated and 45% contained free amine.

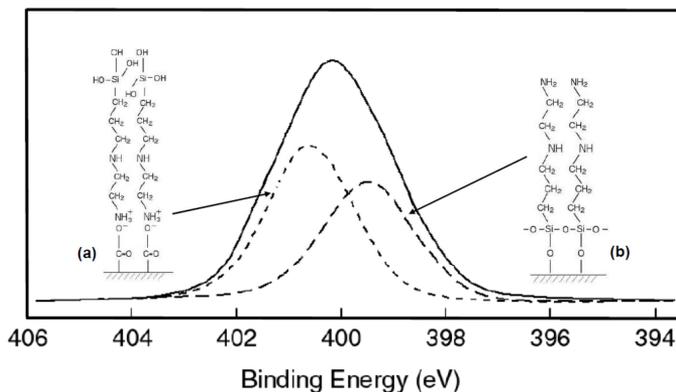


Fig. 6. XPS spectrum of the N 1s peak for the N-(2 aminoethyl)-3-aminopropyl-trimethoxy silane (0.1%) grafted onto onto oxidized LDPE surface [20], including schematic representation of the molecular attachment mechanism and orientation for N-APTMS silane: (a) attachment of silane molecules through protonation of amine with surface hydroxyl groups, i.e. the “amine end down” orientation, and (b) condensation attachment mechanism with “amine end up”

The above observation indicates that both types of amino groups are present in the interphase: (i) Protonated amine groups ($-\text{NH}_3^+$): these are hydrogen-bonded to the oxidized polymer surface, and (ii) Free amino groups ($-\text{NH}_2$), which become available for further reaction with adhesives, matrix resin or other materials.

3.3.2. Adhesion improvement by surface-grafted connector molecules interpenetrating into silicone adhesives

The influence, on adhesion of surface-grafted molecular brushes, interacting with elastomeric silicone adhesives, was investigated using the following materials:

- substrate: EVA/PP blend,
- silicone coating: Silbion 70004/Rhone Poulenc; acetoxo curing system.
- molecular brush system:
 - interpenetrating system: polyethyleneimines (PEI's): MW = 800 ($N = 19$); MW = 2000 ($N = 46$); MW = 25,000 ($N = 581$); MW = 750,000 ($N = 17,442$)
 - chemically bonding system: amino-functional silane: Z-6020.

Adhesion quality was assessed by single lap-shear tests involving the corona treated substrate, surface-grafted with a molecular brush provided by PEI molecules of a varying length ($N = 19$ -17,442) and concentration: 0.1; 0.5 and 1.0%. Z-6020 silane was used at a concentration of 0.1%. Lap-shear specimens were prepared as described in Section 3.2 (10 mm overlap) and cured for 3 days prior to testing: (a) without any exposure, and (b) after 7 days water immersion at 40°C.

The graphs in Figure 7 demonstrate the difference in the relative effectiveness of interfacial reinforcement by interpenetrating or chemical bonding mechanisms. They also illustrate the influence of the type and concentration of interpenetrating graft molecules on the strength of the bonded assemblies. The results indicate that the bond strength of specimens surface modified with interpenetrating molecular brushes (here: PEI) is always greater than that after oxidative treatment only, such as with corona discharge treatment.

An interesting trend is observed here regarding the influence of the length of “connector molecules” on the strength of adhesion. The “bare” interface of an oxidized polymer produces a bond strength of 180 kPa before water exposure. After 7 days water immersion at 40°C, the bonds between the substrate and adhesive are cleaved resulting in a loss of strength through delamination of the adhesive at the interface. For surfaces grafted with interpenetrating only (non reactive) connector molecules of PEI, it appears that increasing the length of the graft chemical molecules results in a corresponding increase in the bond strength, up to approximately 500 kPa for a polymerisation index of $N = 17,442$ and concentration of 0.1%. The exposure of this interface to 7 days water immersion at 40°C results in a 35% loss of strength. An increase in the surface density of the chains, by using higher concentrations of the graft chemicals (0.5% and 1%), also appears to increase bond strengths for PEIs with the higher molecular weights. However despite this increase in bond strength, the failure mode is interfacial delamination, due to the pull-out of interdigitating molecular chains from the matrix of the silicone elastomer.

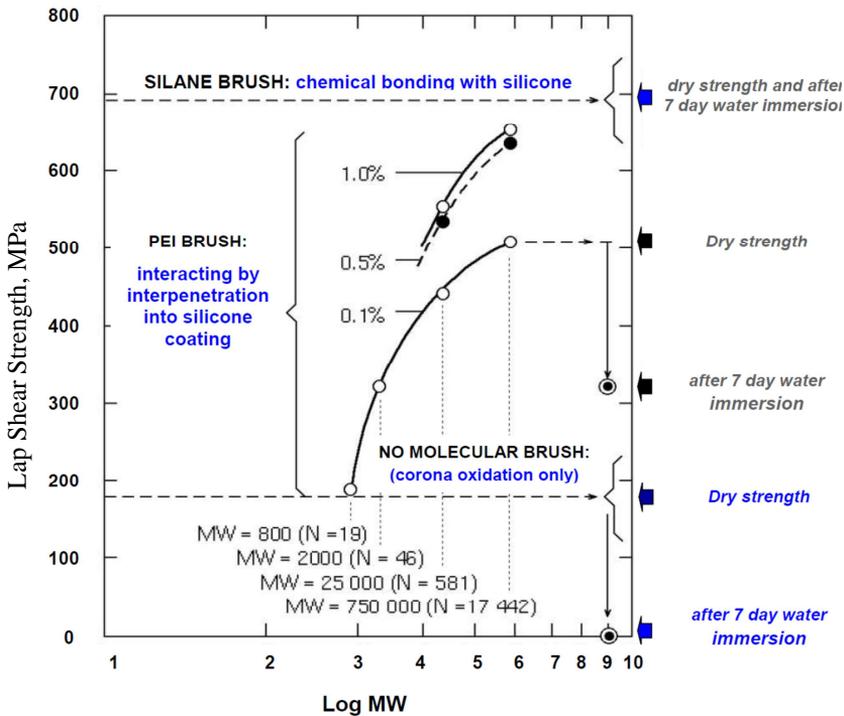


Fig. 7. The influence of PEI molecular weight and chain length ($L \propto N$) and amino-silane Z-6020 on the strength of assemblies involving surface grafted substrates and Silbione silicone coating

When surface grafted “connector molecules” are chemically reactive with the adhesive, as in the case of the amino-functional silane (Z-6020), the highest degree of interphase reinforcement is achieved, up to a level of 690 kPa. This particular interface/interphase system involving chemically bonded “connector molecules” retains its original bond strength of 690 kPa even after 7 days immersion at 40°C.

3.3.3. Adhesion improvement by surface-grafted connector molecules interpenetrating into an elastomeric pressure-sensitive adhesive

The mechanism and effectiveness of adhesion enhancement by the interaction of surface grafted connector molecules with self-adhesive pressure-sensitive tape adhesives was investigated using the the following materials: (1) substrate: PP homopolymer; (2) pressure-sensitive adhesive tape: VHB 4959/3M (acrylic PSA); connector molecules: polyethyleneimines (PEI’s): MW = 800 ($N = 19$); MW = 2000 ($N = 46$); MW = 25,000 ($N = 581$); MW = 750,000 ($N = 17,442$) applied from water-based solution at the concentration of: 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , 0.1, 0.5, 2%.

The quality of adhesion was assessed by peel tests using the specimens and procedure described in Section 3.2. The interface/interphase systems assessed involved PP substrates untreated and surface treated with corona discharge, and those surface-grafted with PEI connector molecules. The key results are illustrated in Fig. 8.

All specimens were conditioned prior to testing: (i) 2 days at temperature of 20°C, and (ii) 12 hours at 60°C in order to provide favourable conditions for enhancing interdigitation of surface grafted” connector molecules” into the matrix of pressure-sensitive adhesive.

All interactions occurring in the experiments illustrated in Fig. 8 are of the van der Waals type only, with the peel strength and corresponding fracture energy increase resulting from the disentanglement and extraction of molecular chains of connector molecules from the cross-linked matrix of the pressure-sensitive adhesive used in these experiments.

It is noticeable from the graph in Figure 8b that almost a linear increase of the bond strength versus N is observed for the length of connector chains in the range of $N = 19$ to 581. Another noticeable feature of this graph is a significant increase of the interface strength observed for the specimens subjected to 60°C conditioning versus 20°C. This observation indicates that the kinetics of the connector chain rearrangements and interpenetration into the matrix of the crosslinked pressure sensitive adhesive constitutes an important part of the mechanism of effective enhancement of adhesion by surface grafted connector molecules. It also indicates that the connector molecules are firmly attached to the substrate surface and hence enable the effective reinforcement of the interface.

Graphs in Fig. 8a illustrate the behaviour of graft chemicals (PEI) grafted from carrier liquid solution at varying concentrations onto the surface of an oxidised PP substrate. According to the theories discussed in [9] the most favourable conditions for the provision of maximised adhesion exist when single macromolecular chains, appropriately separated, are adsorbed and grafted at the polymer surface (see Figure 7 in [9]). The increase of concentration leads to clustering of entangled multiple chains up to the point when excessive amount leads to the creation of a new surface which lacks the ability to interpenetrate into an adjacent adhesive.

It is seen from the graphs in Fig. 8b and c that, in accordance with the earlier discussion, for all connector molecules there is a distinct optimum (σ_{OPT}) in the surface density (σ) of molecular chains which has to be achieved in order to maximize the adhesion between a surface-modified substrate and the adjacent polymeric material.

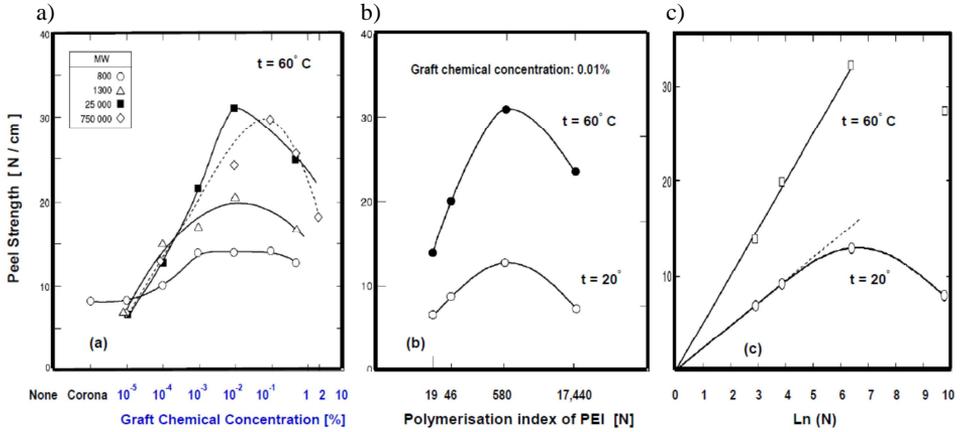


Fig. 8. Influence on the strength of adhesive bonds between PP and elastomeric acrylic PSA adhesive of the following parameters: a) graft surface density (proportional to the PEI concentration) and the length of PEI chains ($L \propto M$; $L \propto N$) at $t = 60^\circ\text{C}$, b) the length of PEI chains ($L \propto N$) grafted onto PP substrate at the constant surface density (relevant to the PEI concentration of 0.01%) at $t = 20^\circ\text{C}$ and 60°C , and c) the length of PEI chains at constant graft chain density

As theoretically determined by de Gennes [1, 2], Léger [15] and Brochard–Wyart [18] and seen from our Fig. 8b and c, a gradual increase in the bond strength occurs with the increasing concentration of graft chemical and the corresponding surface density of grafted molecules for $\sigma < \sigma_{OPT}$, as a result of entanglement of surface-grafted macromolecular chains with the adjacent polymer, in good qualitative agreement with Eqn (6).

For the surface density of grafted macromolecular chains exceeding the optimum concentration (at σ_{OPT}) only partial penetration into adjacent adhesive occurs. It may be considered that the following may be simultaneously occurring: (a) only a fraction of grafted chains fully penetrate into the adjacent polymer; (b) fractional length penetration of some chains occurs; and (c) the network of the adjacent polymer may reject some chain ends.

Our experiments confirm de Gennes [1, 2] theoretical predictions regarding van der Waals interactions of interdigitated connector molecules with the adjacent elastomeric adhesive/polymer.

It is also clear from Fig. 8 that an increase of temperature from 20 to 60°C significantly enhances interpenetration of connector molecules into the matrix of the elastomeric adhesive, as demonstrated by significant increase in the peel strength observed for specimens exposed for 12 hours to an elevated temperature of 60°C . Partial cohesive failure within PSA was visually observed at the best treatment conditions. However, the locus of failure for the other areas is not yet clear, and is being investigated in our current work. The graph in Fig. 8b shows that almost a linear increase of the bond strength versus N is observed for the

length of connector chains in the range of $N = 19$ to 581. The observed increase of the interface strength at 60°C conditioning versus 20°C indicates that: (i) connector molecules are firmly attached to the PP substrate surface and result in an effective reinforcement of the interface, and (ii) the kinetics of the chain rearrangements and interpenetration into the matrix of cross-linked pressure sensitive adhesive are an important part of the effective adhesion enhancement through inter-penetrating connector molecules.

Another observation from graphs in Fig. 8a and c points out to the fact that the length of connector molecules, as relevant to their molecular weight (and degree of polymerisation, “ N ”) for the range of $N = 18.6$ to 17,440 significantly influences the maximum peel strength (and corresponding fracture energy of the interface/interphase system: see Eqn (7)).

The relationship observed has been illustrated in Fig. 8b presenting the maximum peel strength (and corresponding fracture toughness of the interface/interphase system) recorded for each length of “connector molecules” ($L \propto N$) specimens conditioned in temperature 20°C and 60°C from Fig. 8a and c. It is clear from this figure that a well pronounced optimum in the interface reinforcement by surface grafted connector chains occurs at $N = 580$. The strength decrease beyond this point can be attributed to the effect of an entropic barrier to grafting opposing further grafting of any additional connector chains to an existing molecular brush, once the maximum (specific to a particular length of chains) has been achieved.

Although in our experiments discussed in this section we were not able to quantify the surface density of PEI connector molecules [chains/nm²], the arguments similar to the above ones hold in our case due to the fact that σ , in the domain of chain density lower than that associated with the maximum interface strength ($\sigma < \sigma_{OPT}$), should be directly proportional to the concentration of graft chemical in the carrier solution. For concentrations greater than σ_{OPT} , clustering, and for even higher concentrations the formation of a continuous film of adsorbed chemical will commence.

Conclusions

- The adhesion and fracture performance of interfaces between polymers can be effectively improved and controlled by surface grafted macromolecular “connector molecules”.

- “Connector molecules” grafted onto solid polymer surfaces interact with adjacent materials such as adhesives through either one or a combination of the following mechanisms: (i) interpenetration into the adjacent adhesive, and/or (ii) chemical reaction with adhesive.

- The effectiveness of the interface reinforcement by surface-grafted connector molecules depends on the following factors: (i) surface density of

grafted molecules; (ii) the length of the individual chains of the grafted molecules, and (iii) optimum surface density in relation to the length of connector molecules.

- At the interfaces reinforced with interpenetrating connector chains, a distinct maximum/optimum (σ_{OPT}) is recorded for joint fracture energy versus graft density, as expressed by Equation (6). An increase of σ above σ_{OPT} results in a decrease of fracture energy enhancement due to a decrease in the efficiency of the interdigitated macromolecular chains.

- The creation of interpenetrating or chemically reactive molecular brushes by surface oxidation (for example, by flame or corona discharge treatment) followed by the application of polyfunctional connector molecules can be an effective means for significantly improving the adhesion of polymers to elastomeric silicone adhesives.

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