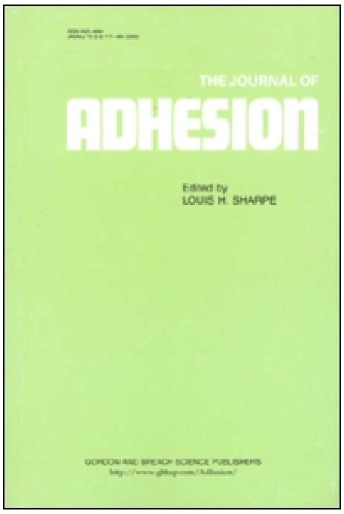

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Interface/interphase engineering of polymers for adhesion enhancement: Part II. Theoretical and technological aspects of surface-engineered interphase-interface systems for adhesion enhancement

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INTERFACE/INTERPHASE ENGINEERING OF POLYMERS FOR ADHESION ENHANCEMENT: PART II. THEORETICAL AND TECHNOLOGICAL ASPECTS OF SURFACE-ENGINEERED INTERPHASE-INTERFACE SYSTEMS FOR ADHESION ENHANCEMENT

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Part I of this paper reviewed the theoretical principles of the macromolecular design of polymer interface/interphase systems for obtaining maximum adhesion and fracture performance of adhesively bonded assemblies. In Part II a novel, relatively simple and industry-feasible technology for surface-grafting connector molecules is demonstrated and discussed in detail and supported by a range of experimental examples. It is shown, in agreement with contemporary theory, that the use of chemically attached graft chemicals of controlled spatial geometry and chemical functionality enables a significant increase in the strength and fracture energy of the interphase, to the point of cohesive fracture of the substrate, or that of an adjacent medium such as adhesive, elastomer, or other material. This occurs even after prolonged exposure of investigated systems to adverse environments such as hot water.

Keywords: Polymers; Surface modification; Adhesion; Adhesive bonding; Fracture energy; Molecular brushes; Adhesives

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INTRODUCTION

Polymers and polymeric composites are becoming increasingly attractive as engineering materials. They are highly competitive with the traditional metals and other alloys due to their low price, excellent processability by high-volume/high-rate techniques such as extrusion and injection molding, and an inherent lack of corrosion-related problems.

Amongst other polymers, polyolefins such as polyethylene, and polypropylene, and their blends with other materials are particularly attractive to industry. The main attributes of these polymers are their low cost, easy processability, low vapour transmission, high impact resistance, and easy recycling.

Various-surface pretreatments, including flame, corona discharge, and plasma treatments, are known to improve the bonding ability of polymers. Most of these processes are oxidative in nature and, with the exception of some types of plasma treatments, they do not graft molecular chains onto the substrate surface. Although the incorporation of oxygenated chemical species onto the surface of the polymer by flame, air corona, or other oxidative treatments is generally sufficient to provide a surface receptive enough for selected adhesives or matrix materials, it is desirable to further improve or optimise the surface properties of a polymeric substrate or reinforcement in composite materials in order to enhance the preferable type of interactions across the adhesive/substrate or matrix/reinforcement interface. Plasma treatment is considered to be the most suitable process currently available for this purpose. The process allows for the incorporation of a wide range of surface chemical species onto the surface of a polymer. 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. Also, in most cases, a plasma treatment can only be used for batch processing. Although continuous plasma equipment has been described in the literature [1], its technological applications are limited to high-value-added products.

POLYMER SURFACE GRAFTING WITH MACROMOLECULAR CONNECTOR CHAINS

A new surface engineering process employing the principles of grafting of macromolecular connector chains developed by CSIRO Australia [2–7] is presented and discussed in this paper.

In this process various polyfunctional chemicals are used as graft molecules. Typical examples of these are

1. long chain bifunctional or polyfunctional macromolecules such as polyfunctional amino-compounds, linear or branched, and
2. short chain bifunctional or polyfunctional compounds capable of forming cross-linked interphases when applied at appropriate concentration, *e.g.*, silanes, titanates, zirconates, or other organo-metallic compounds [2, 4–7].

The untreated (as received) polymeric materials are not reactive with bifunctional or polyfunctional graft chemicals such as polyfunctional amines, silanes, or other coupling agents in terms of reactivity through hydrogen bonding or covalent bonding, due to the absence of the required surface chemical functionalities at the substrate surface. This deficiency can be overcome by an oxidative treatment of the polymer surface in order to provide appropriate receptive sites, *e.g.*, OH, C=O, COOH, capable of chemically interacting with functional groups available at the ends or branches of connector molecules. The process discussed in this paper comprises the following:

1. Surface oxidative treatment by a physical and/or physico-chemical means, *e.g.*, flame, corona discharge, ozone, or UV treatment.
2. The application of a silane, organo-metallic, or other polyfunctional chemical containing the atomic species/molecules capable of creating hydrogen, ionic, or covalent bonds with the appropriate receptive groups on an oxidised polymer surface.

As outlined in Gutowski [9], a certain critical surface density of macromolecular chains needs to be grafted onto the surface for maximising the performance of the interphase. To facilitate this, the polymer surface first needs to be oxidised at a required energy input, E, determined by the following expression:

$$E = P\,t\,n, \tag{1}$$

where P is the power output (Watts) of the energy source, *e.g.*, corona discharge electrodes or flame burner; t is the time of exposure of the substrate length unit under the electrode or flame cone of width, d (mm) (time $= d/V$, where $V =$ treatment velocity of the substrate versus energy source (mm/s)); and n is the number of substrate passes under the energy source.

The energy output (mJ/mm^2), E_u, per unit of the substrate surface area is:

$$E_u = \frac{Pn}{LV}, \tag{2}$$

where L is the length (mm) of the treating electrode, flame burner, or other energy source.

The process discussed in this article provides an easy means for the grafting of a wide range of surface macromolecular chains, terminated with desired functional groups, onto the surface of a polymeric substrate. The latter can be easily perceived from Figure 1a, which schematically illustrates the process involving the following: surface oxidation of a PE substrate by corona discharge or flame treatment, and spray-application of an amino-functional silane.

Macromolecular or short-chain graft chemicals (see section "Connector Chains," below for details) are applied onto the surface of an oxidised substrate by means of dipping, spray, vapour deposition, printing, or other known deposition technique. In this work, the graft chemicals are applied by dipping in or spraying of an appropriately diluted solution (see section "Procedures and Process Configuration for Surface Grafting Connector Chains," below, for details). Figure 1 provides a schematic illustration of the process described and analysed in this paper.

The chemical functionality of end-groups or branches on compounds used as connector molecules, as illustrated in Figure 1b, is chosen to provide a chemical reactivity compatible with that of the adhesive,

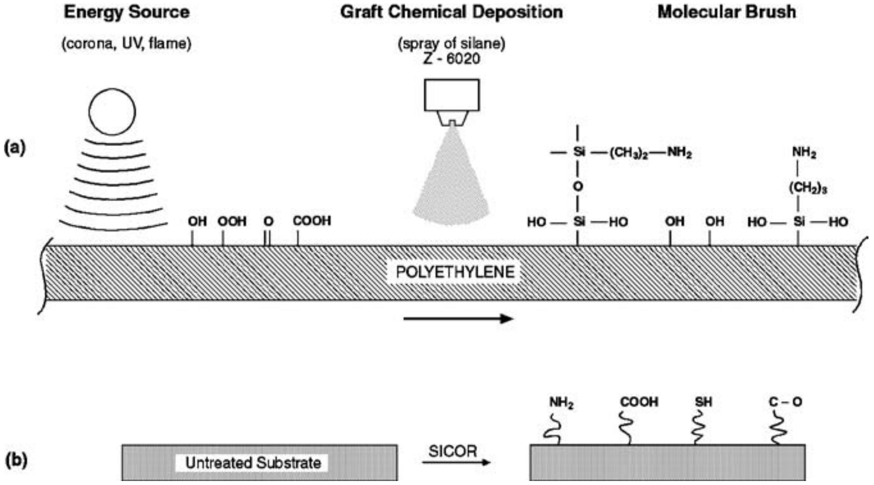


FIGURE 1 Schematic representation of the SICOR process: (a) schematics of surface grafting of molecular brushes for controlled interphase/interface performance onto polyethylene substrate; and (b) examples of end-group chemical functionalities.

composite matrix or other material to be brought into contact with a polymer surface modified with reactive graft chemicals.

It can be seen from the above, and will be discussed in the later part of this work, that the process provides a relatively simple means of online tailoring of the surface chemistry of a polymer without altering its bulk properties.

EXPERIMENTAL

Methods

Substrate Oxidation

In our experiments, surface oxidation of polymeric substrates was carried out alternatively by the use of flame or corona discharge treatment.

Corona discharge treatment equipment. Corona discharge treatment was carried out using the Tantec EST System HV 2010 (Lunderskov, Denmark): power output, 1 kW (maximum), output frequency, 13–30 kHz.

The system comprises the following main units:

- High frequency generator HV 2010–240 V/50–60 Hz
- High voltage transformer HT 10–28 kV output
- Treatment speed 0.1–70 m/minute

In this work, the distance between the substrate surface and electrode was maintained at 2.5 mm, whilst the treatment speed and energy output were controlled to achieve the energy output (see Equation (2)), E_u, of 20 mJ/mm^2 to 755 mJ/mm^2.

Flame treatment equipment. Flame treatment was carried out with commercially available equipment manufactured by Aerogen Company (Alton, UK). The unit used in this work was an Aerogen FT Lab model equipped with a 200 mm long AT 533 burner, providing a maximum energy output of 35.1 kW, *i.e.*, 1.755 kW/cm length (120,000 BTU/hour).

All flame treatments were carried out with stoichiometric air/propane mixture exhibiting 1% oxygen excess in afterburn mixture, unless indicated otherwise. During treatment, one side of the polymeric substrate was exposed to a laminar premixed flame. The treatment distance (between the flame tip and substrate surface) could be adjusted from 5–130 mm. In this work, a standard distance was maintained at 10 mm. The treatment speed was adjustable within the range 20–84 m/minute. In this work, the standard treatment speed was 60 m/minute.

Ammonia Plasma Treatment

Low density polyethylene (LDPE) and polypropylene (PP) were subjected to plasma treatment, which was carried out in the laboratories of CSIRO Molecular Science, Melbourne, Australia, using equipment built in-house. Ammonia was used as the process gas. The system was evacuated to a pressure below 0.05 Torr, before ammonia gas was fed into the reactor at a flow rate of $5\,\mathrm{cm}^3$/minute. Once a constant pressure of 0.6 Torr was achieved, plasma was generated by an oscillator operating at 700 kHz, with a power input of 35 W for 60 s for both LDPE and PP samples discussed in this paper.

Preparation and Application of Graft Chemicals

Silanes were first hydrolysed with distilled water with a pH of 5.9 without additional adjustment of the solution's pH at 1:3 (silane: water) mole ratio for 24 h. The hydrolysed silanes were then diluted with water or isopropanol to obtain 0.05 to 1% solutions.

Other graft chemicals were directly diluted in demineralized water (conductivity below $18 \times 10^6\,\Omega\,\mathrm{cm}$) to obtain the required concentration. The standard concentration of chemical solutions throughout most experiments, industrial trials, and subsequent production was 0.25%.

Procedures and Process Configuration for Surface Grafting Connector Chains

Laboratory Procedure

The substrates, oxidised 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 drying in an oven at 40°C. The dip in a solution of chemical was subsequently replaced by an online spray application. This was carried out immediately after corona discharge or flame oxidation, followed by a flash-off implemented by an infrared drying element placed above the conveyor.

Pilot Plant and Industrial-Scale Procedures

The substrate samples or full-size plastic components were treated using an online SICOR unit (prototype equipment built in-house at CSIRO Manufacturing & Infrastructure Technology/Melbourne, Australia) comprising the following main subsystems and procedures (see Figure 1a for schematic illustration):

1. Flame treatment: 60 m/min
2. Graft chemical solution spray: 10 mL/min flow rate
3. Graft chemical solution residence: 20 s (to enable adsorption and attachment of graft chemical macromolecular chains onto receptive sites created by polymer oxidation)
4. Infrared or hot air flash-off: 4 min at 80°C.

Materials and Methods

Substrates

The following engineering polymers were used in our experiments and at various stages of the process scale-up and appraisal: low density polyethylene (LDPE); high density polyethylene (HDPE); polypropylene (PP); ultra-high molecular weight polyethylene (UHMW-PE). All substrates used were 3 mm thick.

Adhesives and Elastomeric Sealants

The adhesives and sealants used in this work were single (1-P) or two-component (2-P) packs and were used in accordance with the manufacturer's specifications. This included curing at laboratory conditions (20 ± 2°C; RH = 55 ± 5%) for 3 days, unless specified otherwise, prior to testing or subjecting the specimens to any exposure, *e.g.*, water immersion.

Adhesives: structural acrylic (1-P): Permabond F-241 (Permabond, Hampshire, UK)
cyanoacrylate (1-P): Loctite 406 (Loctite, Rocky Hill, Connecticut, USA)
structural epoxy (2-P): K-138 (Ciba Geigy, Basel, Switzerland). Epoxy resin: cross-linker ratio = 10:4 (by weight)
structural polyurethane (2-P): 7520 A/B (Lord Corporation, Erie, Pennsylvania, USA)
Elastomeric adhesives (silicone): Silbione 70004 (1-P) (Rhone-Poulenc, Lyon, France)—3-day cure
Elastomeric self-adhesive tapes: VHB 4959 (3M, St. Paul, Minnesota, USA)

Macromolecular "Connector Chain Molecules"

Organo-functional silanes:

- N-(2 aminoethyl)-3-aminopropyltrimethoxysilane: Z-6020 (Dow Corning, Midland, Michigan, USA).

- 3-glycidoxypropyltrimethoxysilane: Z-6040 (Dow Corning).
- γ-aminopropytriethoxysilane: A-1100 (Union Carbide/Witco Corp., Danbury, Connecticut, USA)

Polyfunctional amines:

- Polyethylene imines (PEI): MW (weight average) = 800; 2000; 25,000; 750,000: BASF (Ludwigshafen, Germany & Rensselaer, New York, USA)

The chemical structures of representative macromolecular connector molecules used as graft chemicals in this work are illustrated in Figure 2.

Experimental Procedures

XPS X-Ray Photoelectron Spectroscopy Analysis

XPS analyses were performed on a VG Escalab MkII spectrometer (Vacuum Generators, UK) equipped with an Al K_α source, nonmonochromatised, at a power of 150 W. Samples were exposed to irradiation for less than 30 min to avoid substantial decomposition of the polymer surfaces in the analysis beam. Spectra were recorded at normal emission of the photoelectron relative to the surface plane of the samples (0°). The spectrometer did not provide for charge neutralization. For a nonmonochromatised X-ray source, shifts are usually uniform across the surface and invariant with time due to a stable charge balance almost instantaneously established on the specimen.

Elements present were identified from survey spectra, and the atomic concentrations were estimated from integrated peak intensities and published sensitivity factors [10]. Components of the C 1*s* signal were estimated by curve fitting using Gaussian-Lorentzian line shapes and a nonlinear background subtraction. The binding energy scale was calibrated using a value of 285.0 eV for the CH_2 component as an internal reference. The random error in the quantitative analysis of elemental compositions is between 5% and 10% in the present cases.

FTIR Analysis

A Fourier transform infrared spectrophotometer, BIO-RAD FTS-7R1 (Bio-Rad Laboratories, Digilab Division, Cambridge, Messachusetts, USA), equipped with a $LiTaO_3$ detector, was used at a resolution of 4 cm^{-1} to collect infrared spectra of LDPE surfaces prior to, and after, various surface treatments. All spectra were obtained with the aid of a 4 × variable ATR and beam condenser accessory with

N - (2-aminoethyl) - 3 - aminopropyltrimethoxy silane

$NH_2 CH_2 CH_2 NH(CH_2)_3 Si(OCH_3)_3$

(a)

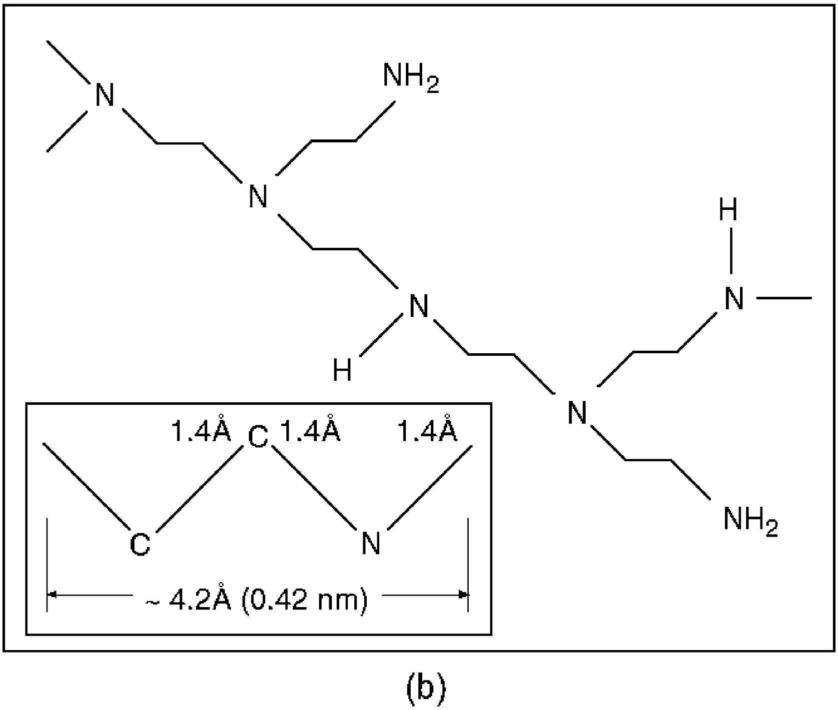


FIGURE 2 Chemical structures of representative connector molecules used as graft chemicals in this work: (a) N-(2 aminoethyl)-3-aminopropyltrimethoxy silane; and (b) polyethylene imines.

KRS-5IRE crystal (10 × 5 × 1 mm). The incident angle was fixed at 45° and the specimens were cut into two pieces to cover each side of the reflective surface to increase the sensitivity of the analysis. A constant torque was used during installation of the specimens to minimize the technique's susceptibility to differing contact between the sample and the crystal. Generally, the background spectrum collected in air, and the single beam spectrum of the polymer sample, were obtained by coadding 64 scans.

Adhesive Bonding and Assessment of Bonded Assembly Performance

Strength Determination

All specimens were tested in an Instron mechanical tester Model 5565 (Instron, Canton, Massaclusetts USA) at a rate of 10 mm/min. Five specimens were tested per experimental point. Various load cells (100 N, 500 N, 1000 N, and 5000 N) were used, depending on the force required to stress the specimens to failure. In all cases, the load cell sensitivity was ±0.5%. All mechanical testing was carried out at $T = 20 \pm 2\,^\circ\mathrm{C}$ and RH $55 \pm 5\%$. The standard deviation of all experimental results was within the range ±5–10% of the mean value (consequently, no error bars are indicated in Figures 10–19, in order to keep the graphs clearer).

Specimen Preparation and Test Procedure

Tensile specimens bonded with pressure-sensitive adhesive (PSA) tapes. The strength (MPa) of bonds was determined by relating the maximum load ($F_{\max}$) to the effective bond area (A) using 50 × 25 mm cross-lap specimens (see Figure 3) and adhesive tape squares, 21 × 21 mm for VHB 4959 tape. As recommended by 3 M specifications, the specimens were prepared by applying self-adhesive tape to the

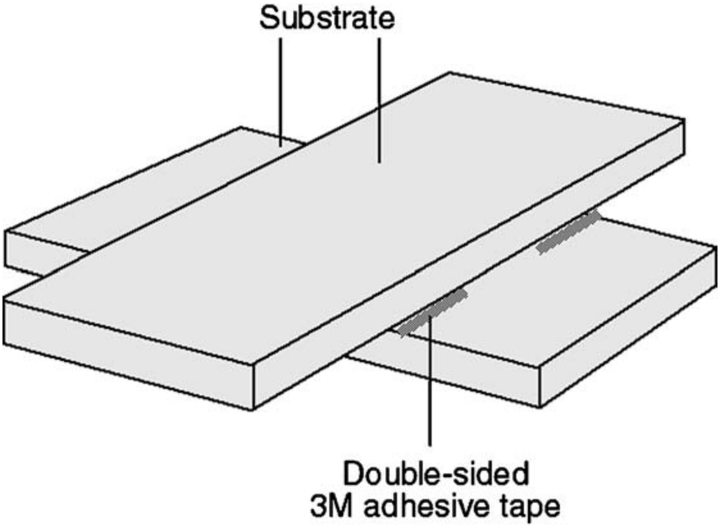


FIGURE 3 An illustration of a cross-lap specimen used for determining the tensile strength of self-adhesive double-sided tapes and elastomeric adhesives (sealants).

substrates followed by passage of a 6.8 kg roller. Subsequently, bonded specimens were allowed to condition for 3 days at $T = 20\,^{\circ}\mathrm{C} \pm 2\,^{\circ}\mathrm{C}$ and $\mathrm{RH} = 55 \pm 2\%$ prior to testing and/or any further exposure, e.g., water immersion.

Tensile specimens bonded with elastomeric sealants. Tensile specimens, as illustrated in Figure 3, with $25 \times 10 \times 1.4$ mm sealant beads, were prepared and allowed to cure for 3–14 days prior to testing (see section "Adhesives and Elastomeric Sealants," above, for cure time of relevant sealants). The strength (MPa) was determined by relating the maximum load ($F_{\max}$) to the effective bond area (A).

Lap-shear specimens and shear strength determination. The shear strength (stress at failure in MPa; *i.e.*, $\mathrm{N/mm^2}$) was determined using single lap-shear assemblies (variation in test method derived from ASTM D3165–73), 25 mm wide with an overlap of 3 mm. This overlap was chosen in order to avoid the substrate failure that occurred with the standard 5 or 10 mm overlaps. All substrates were cleaned with isopropyl or ethyl alcohol prior to any further treatment.

Peel specimens, peel strength, and fracture energy determination. The peel strength (in N/cm width of the specimen) was determined using 180° peel specimens (100 mm long and 20 mm wide) that were prepared in accordance with ASTM C-794 [11]. The fracture energy can be simply estimated by the use of Equation (3):

$$G_c = \frac{F_c}{b}(1 - \cos\alpha), \tag{3}$$

where F_c is peel force, b is the width of the peel specimen, and α is the peel angle.

The top of peel specimens involving silicone sealant layer was reinforced with a SICOR-modified 0.1 mm thick PP film to minimise sealant stretching during peel tests. The sealant thickness was reduced [12] from the standard-recommended 1.6 mm to 0.2 mm in order to enhance interfacial failure in favour of cohesive failure within the relatively weak silicone sealants, when inherent adhesion problems were present.

The top of peel specimens involving pressure-sensitive adhesive tape VHB 4959/3M was reinforced by 3M self-adhesive tape 3M 981, which is reinforced with glass fiber strands to prevent tape stretching during peel tests. A 100 N capacity (sensitivity ±0.5%) load cell was used during testing. The variability of recorded peel force was ± 5–8% of the mean value, along the whole peeling path of 75 mm.

While it is known that the fracture of the majority of polymeric materials, such as rigid or elastomeric polymers and that of interfaces involves many irreversible processes associated with macroscopic deformations that dissipate energy from the applied stress, *e.g.*, plastic yielding, bending, and other sources, we assume that the sum of these viscoelastic losses, Ψ, is constant throughout our experiments, and hence all results are comparable with each other. To ascertain the above, all peel tests were carried out at the constant speed of 10 mm/min at a temperature of 20°C ± 2°C. The dimensions and structure of all peel specimens were identical throughout whole sets of experiments.

RESULTS AND DISCUSSION

Surface Chemistry of Selected Polymers After Various Types of Surface Modification

Due to the broad range of polymeric substrates and graft chemicals used as "connector molecules" within the scope of this work, the surface chemistry aspects of various processes are discussed briefly using the following representative processes and materials:

1. Surface oxidation: LDPE.
2. Ammonia plasma: LDPE and PP.
3. Surface grafting (oxidation and graft chemicals: Z-6020 silane and PEI).

Surface "Receptivity" of Unoxidised LDPE

As outlined in the section, "Polymer Surface Grafting with Macromolecular Connector Chains" above, the surfaces of unoxidised (as received) polymers are not receptive to silanes or other graft chemicals in terms of reactivity through hydrogen or covalent bonding, due to the absence of the required surface functionalities, *e.g.*, OH or COOH. This lack of receptivity of untreated LDPE is clearly demonstrated by the comparison of Fourier transform infrared (FTIR) spectra illustrated in Figure 4 [6], which demonstrates that the film of a physisorbed γ-APS deposited from a 0.1% solution in isopropyl alcohol (see Figure 4a) is removed by rinsing with water or isopropanol, as indicated by spectrum (b) in Figure 4.

Some residual silane retention after the isopropanol wash can be observed by the presence of a small peak near 1100 cm^{-1}, characteristic of Si$-$O$-$Si bonds.

This residual presence of chemisorbed silane can be explained using the results of XPS analysis that shows the presence of a small quantity of oxygen in the spectrum of untreated LDPE (result not shown in

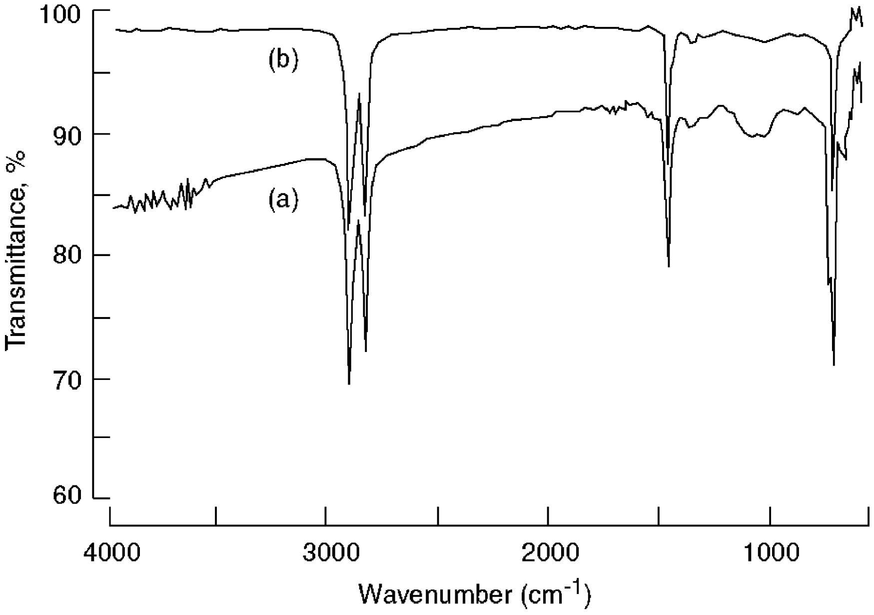
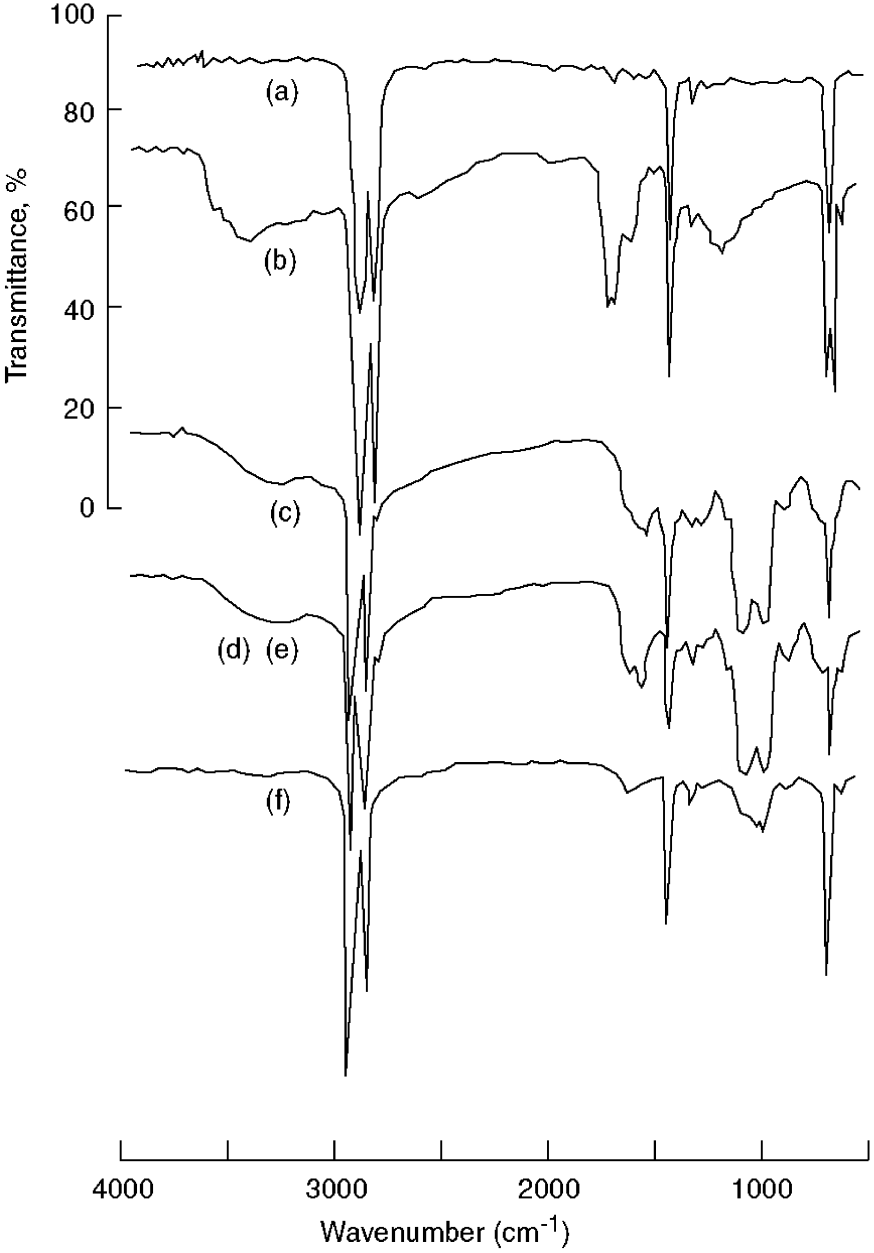


FIGURE 4 FTIR-ATR spectra of LDPE primed with 0.1% solution of γ-APS in isopropyl alcohol without any polymer pretreatment (*e.g.*, corona discharge) prior to silane deposition: (a) LDPE with physisorbed γ-APS; and (b) the same specimen after rinsing with water or isopropanol [6]. From Gutowski, W., Wu, D. Y., and Li, S., *The Journal of Adhesion*. (Copyright (1993) Reproduced by permission of Taylor & Francis, Inc., http://www.routledge-ny.com).

this paper). One hypothesis is that some quantity of silane could be adsorbed through acid-base interactions between these surface-oxygenated species and silane molecules. The presence of this residual silane, however, does not have any beneficial effect on the bond strength, since adhesive bonds prepared using untreated LDPE substrate primed with silane solution and then rinsed with isopropanol prior to bonding are so weak that they delaminate during specimen fixing in the grips of a mechanical tester.

Surface Grafting of Amino-Silane Connector Molecules to Oxidised LDPE

The creation of appropriate oxygenated species such as OH or COOH on the surface of a polymer such as LDPE, through the application of corona discharge or other oxidative processes, provides receptive sites capable of forming either hydrogen, ionic, or covalent


100
80
60
40
20
0
Transmittance, %
(a)
(b)
(c)
(d)
(e)
(f)
4000
3000
2000
1000
Wavenumber (cm^{-1})

bonds with reactive functional groups of graft chemicals. The viability of such a mechanism is demonstrated through the analysis of the FTIR spectra of surface-modified LDPE in Figure 5. Spectrum (b) in Figure 5 represents the surface of corona discharge-(755 mJ/mm^2) oxidised LDPE.

It can be seen that the following specific absorption bands [6] appear in the spectrum of corona discharge-oxidised LDPE.

1. $3300\,cm^{-1}$: this absorption band can be assigned to OH hydroxyl groups. The XPS analysis of the same sample indicated, however, the presence of a small quantity of nitrogen (N(l*s*) peak) at the surface. It is thus likely that the broad band at $3300\,cm^{-1}$ can be attributed not only to the stretching vibration of hydrogen-bonded OH, but also to residual NH and NH_2.
2. $1720\,cm^{-1}$: characteristic of carbonyl groups (C=O).
3. $1630\,cm^{-1}$: characteristic of ether: double bonds (C=C) or amino groups (NH_2).
4. $1200\,cm^{-1}$: characteristic of ether-functional groups (C–O).

Spectrum (c) in Figure 5 relates to LDPE surface grafted with amino-functional silane (γ-APS) molecules, subsequent to oxidation by corona discharge treatment at $755\,mJ/m^2$. The analysis of this spectrum reveals the following characteristic absorption bands [6].

1. $3300\,cm^{-1}$: assigned to a mixture of OH, NH, and NH_2 hydrogen-bonded stretching vibrations.
2. $1650\,cm^{-1}$: assigned to amine deformation mode of acceptor amine groups involved in strong hydrogen bonding.
3. $1590\,cm^{-1}$: assigned to the mixture of primary and secondary NH bonds.
4. 1130 and $1035\,cm^{-1}$: assigned to Si–O–Si and SiOH band, respectively.
5. $930\,cm^{-1}$: assigned to the SiO stretching mode of silanol [14].

FIGURE 5 FTIR-ATR spectra of LDPE subjected to the following treatment: (a) untreated (as received) LDPE; (b) surface-oxidised LDPE (corona discharge at $755\,mJ/mm^2$); (c) amino-grafted LDPE (0.1% γ-APS on oxidised surface of LDPE); (d) sample (c) after 1 week immersion in isopropanol; (e) sample (c) after 2 months immersion in isopropanol; and (f) sample (c) after 2 months immersion in water [6]. From Gutowski, W., Wu, D. Y., and Li, S., *The Journal of Adhesion*. (Copyright (1993) Reproduced by permission of Taylor & Francis, Inc., http://www.routledge-ny.com).

The absence of the carbonyl absorption band at 1720 cm^{-1} (originally present at the oxidised LDPE surface) is explained by the formation of bonds between the carbonyl groups on the polymer surface and the amino and/or hydroxyl groups of the hydrolized silane molecules, which, consequently, would lead to the shift of the band initially located at 1720 cm^{-1} to about 1650 cm^{-1}, where the hydrogen-bonded amine deformation mode also appears [6].

The FTIR analysis of γ-APS-grafted LDPE surfaces subjected to prolonged immersion in isopropanol and water provides an interesting insight into the structure and hydro-thermal stability of the interphase.

A small but noticeable difference between the spectra of freshly-grafted (see Figure 5c) and isopropanol-aged surfaces can be seen by comparing the spectrum shown in Figure 5c with those illustrated in Figures 5d (1 week immersion) and 5e (2 months immersion) in the range of 1500–1560 cm^{-1} and near 1300 cm^{-1}. These changes may be associated with several phenomena, *e.g.*, further removal of some originally attached surface species, reorientation of surface-functional groups, and/or formation of internal hydrogen bonds between closely located functional groups.

Spectrum (f) in Figure 5 reflects noticeable changes to surface chemistry of amino-silane-grafted LDPE subsequent to 2 months immersion in water. The major differences in surface chemistry of grafted LDPE subjected to 2 months water immersion in comparison with freshly grafted or isopropanol-aged surfaces can be explained by the displacement by water of some silane molecules, hydrogen-bonded to the oxygenated polymer surface through either –OH groups or NH_2 groups, which were not displaced by the less polar isopropanol. This phenomenon is evidenced by the disappearance of bands at 1035 and 1130 cm^{-1}. The two absorption bands at 1190 and 1135 cm^{-1} which are not removed by water are attributed to the chemically bonded silane or hydrogen-bonded Si–O–Si oligomer from the condensation of hydrolysed methoxy silane. Another absorption band at 930 cm^{-1}, not removed by water immersion, is attributed to SiOH [13]. Again, the absence of the carbonyl band at 1720 cm^{-1}, originally present in the corona discharge only treated LDPE (see spectrum (b) in Figure 5), together with the presence of the 1650 cm^{-1} band in the IR spectra of the material aged in water after original silanisation (Figures 5c and 5d), can be interpreted as the shift of the band from 1720 to 1650 cm^{-1}, resulting from the formation of bonds between carbonyl groups of the polymer surface and amino and/or hydroxyl groups of the silane molecules [6]. The peak at 1590 cm^{-1}, which is assigned to free primary or secondary amine, has also disappeared after immersion in water, while the absorption band of the amino group strongly hydrogen-bonded at 1650 cm^{-1} remains unchanged.

It can be postulated, based on the above observations, that the interfacial layer of grafted amino-functional silane (0.1% γ-APS) comprised both chemisorbed molecules firmly attached to the oxidised polymer surface through chemical bonds, as well as physisorbed molecules that reside on the outermost layer of the silane-based interphase. The latter were easily cleaved from the surface by washing with water, whilst the chemisorbed silane molecules are retained at the original attachment sites, even after 2 months immersion in water.

Ammonia Plasma-Treated LDPE and PP

A detailed analysis of surface chemistry of ammonia plasma-treated polyolefins (LDPE; HDPE, and PP), identical to those used in this work, has been provided by Wu *et al.* [14]. In this paper, we provide only general information, extracted from earlier work [6, 14], as relevant to the context of this current work.

The XPS analysis of ammonia plasma-treated LDPE and PP (see Wu *et al.* [14] for detailed analysis) reveals the presence of substantial signals assignable to nitrogen (N 1*s*) and oxygen (O 1*s*). The results of

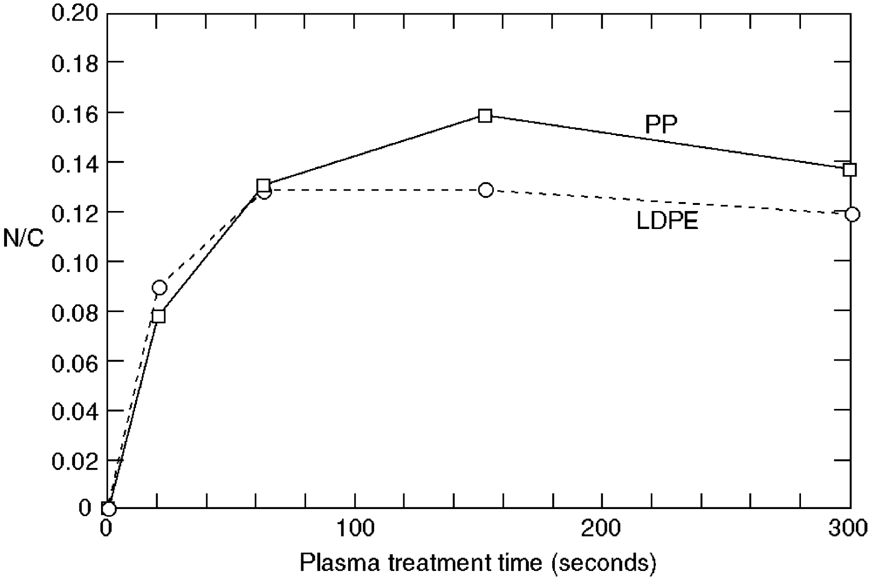


FIGURE 6 Effect of ammonia plasma treatment time on (N/C) elemental ratios for LDPE and PP treated at a power output of 20 W.

analysis related to (N/C) elemental ratio, based on data published earlier [14], are illustrated in Figure 6.

Spatial Orientation of Surface-Grafted Connector Chains

Amino-Functional Silane

The structure of surface-grafted amino-functional silane on the oxidised polymer surface can be schematically illustrated in the simplified model shown in Figure 7. The configuration of free-standing brushlike silane molecules (Figure 7a) is applicable to the relatively low surface density of reactive attachment sites, while the dense and cross-linked silane interphase/interface model (Figure 7b) represents more a surface containing rich functionality. The real surface configuration is expected to be far more complex considering that the surface grafting can be affected by many factors, such as the self-condensation

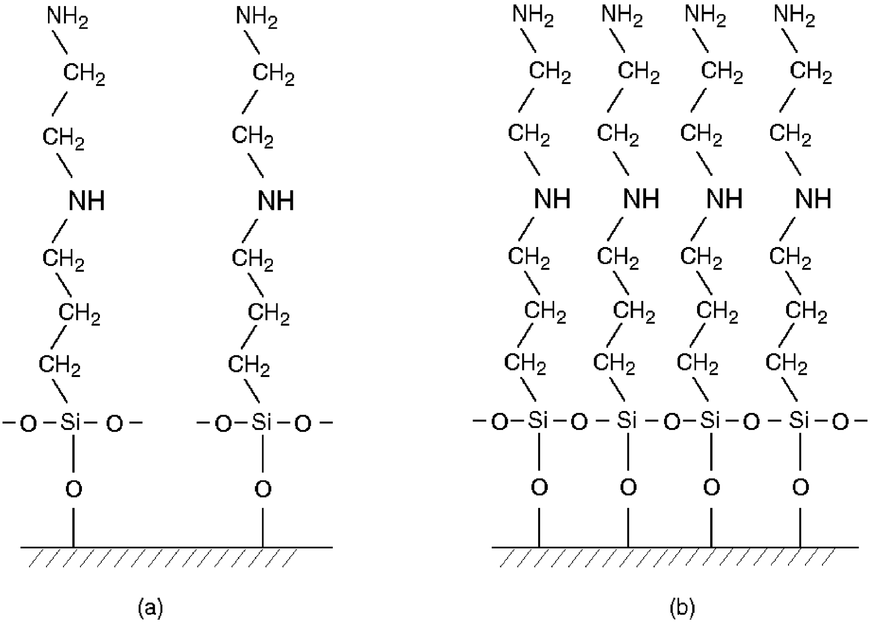


FIGURE 7 Schematic representation of the molecular attachment mechanism in the "amine-end up" orientation for the N-(2 aminoethyl)-3-aminopropyltrimethoxy silane: (a) individual, free-standing silane molecules spaced at the distance preventing the formation of a continuous cross-linked polysiloxane layer, (b) condensation attachment mechanism with surface-grafting density enabling condensation of adjacent Si-OH units.

reaction of silane and any surface defects. Compared with metal or silica surfaces, very little work on polymers has been carried out, and the chemical reactions on the polymer surface are less clear. On the oxidised polymer surface, the reaction of the silanol-end with the surface -OH or the amine group of silane with -COOH are possible, but strong hydrogen bonding between silane and the surface-oxygenated functionalities cannot be excluded. Due to the lack of appropriate analytical tools available to us we are not able, at this stage, to determine the threshold value of surface density, σ, of surface hydroxyl and/or carboxyl groups required to achieve surface-grafting configuration as represented by the model illustrated in Figure 7b, or to determine the true surface configuration of grafted molecules in this work.

Figure 8 illustrates the XPS spectrum of the N 1*s* peak of the γ-APS silanised LDPE. Two components of the N 1*s* peak were observed near 399.3 and 400.4 eV, which were attributed to free and protonated amino groups, respectively. Based on the relative intensities of the two components, it turned out that about 55% of the amino-silane was protonated and 45% contained free amine.

The above data indicate that both types of amino groups are present in the interphase:

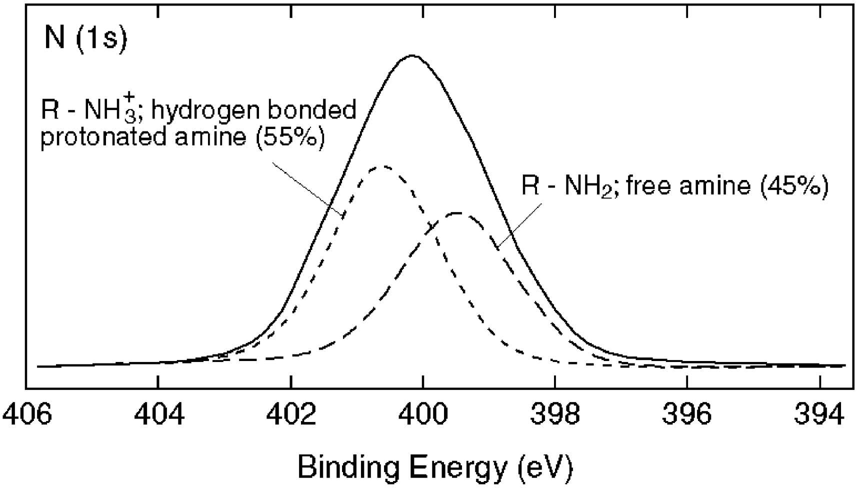


FIGURE 8 XPS spectrum of the N 1*s* peak of the γ-APS silane (0.1%) grafted onto oxidised LDPE surface [6]. From Gutowski, W., Wu, D. Y., and Li, S., *The Journal of Adhesion*. (Copyright (1993) Reproduced by permision of Taylor & Francis, Inc., http://www.routledge-ny.com).

1. protonated amine (NH_3^+) or amine hydrogen-bonded to the oxidised polymer surface; and
2. free amino groups (NH_2), subsequently available for further reaction with adhesives, matrix resin, or other materials.

The strong interaction of ionic bonding or hydrogen bonding between the grafted silane and the polymer surface, and between the inter- and intra-molecules of silane can reinforce the interfacial mechanical properties, while the free amine is available for further reaction with adhesives or other coatings. These combinations can lead to an improvement of bonding strength, as shown later on.

Polyethylene Imines

The chemical structure of polyfunctional amines (polyethylene imines: PEIs) used in this work as surface-grafted macromolecular connector chains is illustrated in Figure 2b. These chemicals are used in our experiments in a broad range of average molecular weights, *i.e.*, $MW = 800$ ($N = 19$), $MW = 2000$ ($N = 46$), $MW = 25{,}000$ ($N = 581$), and $MW = 750{,}000$ ($N = 17{,}442$).

Considering the branched structure (see Figure 2b) of macromolecular chains of PEIs and their considerable length, it is postulated (although we are not able, at this stage, to provide structural data to confirm the above) that at longer chains (higher MW) they are adsorbed and grafted onto the surface through multiple amine groups

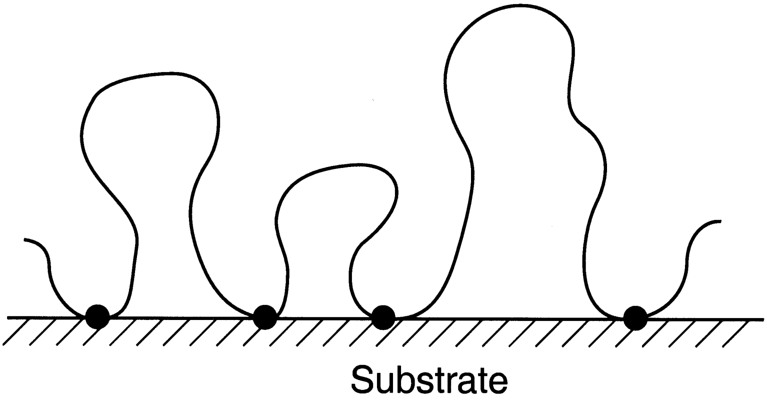


FIGURE 9 Idealized representation of a long-chain polyethylene imine (PEI) attached to the oxidised polymer surface through a number of contact points resulting from reaction between surface carboxyl groups and amine groups available at multiple branches along the main chain of PEI. Note that for simplicity we do not show the branched structure of PEI in this figure.

available at the chain's branches, and form the looped structure schematically illustrated in Figure 9. Note that, for simplicity, we do not show the branched structure of PEIs in this figure.

Adhesive Bonding of Engineering Plastics

Surface-Grafted Connector Molecules Chemically Reactive With the Adjacent Adhesives

The effectiveness of adhesion enhancement between polymeric substrates and a range of rigid, cross-linked adhesives by surface-grafted molecular brushes that are reactive with these adhesives was verified using LDPE, PP, HDPE, and UHMWPE, and assessed by single lap-shear tests.

Figure 10 illustrates the relationship between the strength of the bond, and the energy output of the corona discharge generator during

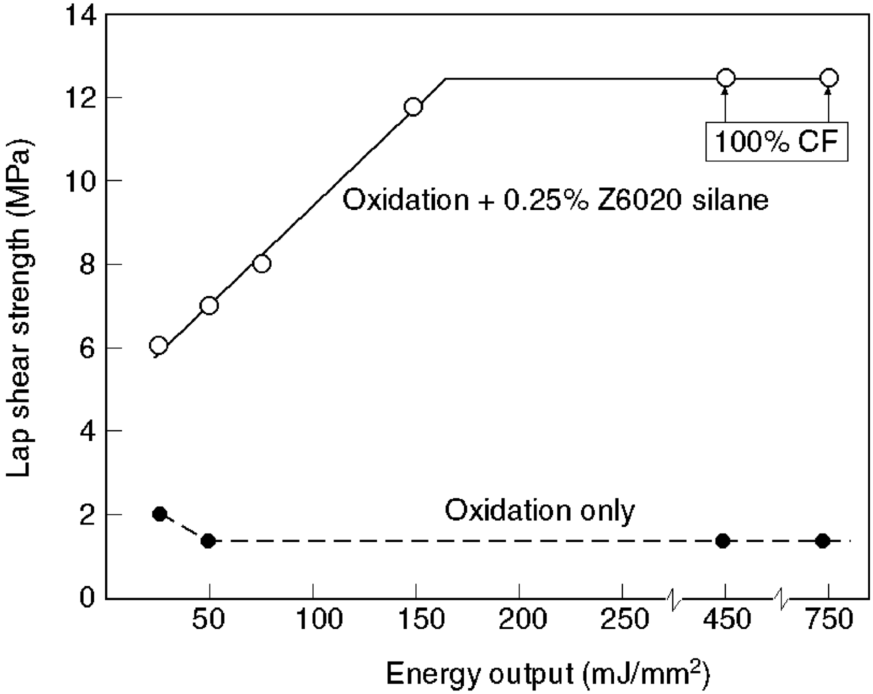


FIGURE 10 The relationship between the strength of adhesive bond and the energy output of the oxidative corona discharge used for activating the surface of HDPE substrate (incorporation of reactive OH and COOH sites) prior to grafting amino-silane and bonding substrates with a chemically reactive cyanoacrylate adhesive (Loctite 406).

surface oxidation of HDPE substrate. It is seen from this figure that the increasing energy output during HDPE oxidation (which is thought to lead to the increased surface density of OH and COOH groups on the HDPE surface) results in the linear increase in the bond strength in the systems involving HDPE substrates surface-grafted with amino-functional graft molecules chemically reactive with the cyanoacrylate adhesive. It has been observed in our experiments that all data points located on the ascending part of the graph represent the specimens exhibiting 100% delamination of the adhesive from the substrate, whilst those located on the plateau (at 450 and 755 mJ/mm^2 energy output) exhibit 100% cohesive fracture within the polymer.

Figure 11 compares the strength of lap-shear specimens involving LDPE, PP, HDPE, and UHMWPE substrates, untreated and surface-treated with corona discharge, and those surface-grafted with silane connector molecules (amino-functional silane, Z-6020, at the concentration of 0.25%).

The untreated or treated specimens were bonded with a range of adhesives: cyanoacrylate, acrylic, epoxy, and polyurethane.

It is clearly seen from the graphs in Figure 11 that the strength of bonded assemblies with specimens surface-engineered with connector molecules provided by surface-grafted amino-functional silane Z-6020 is always significantly greater than that after oxidative treatment such as corona discharge or flame treatment.

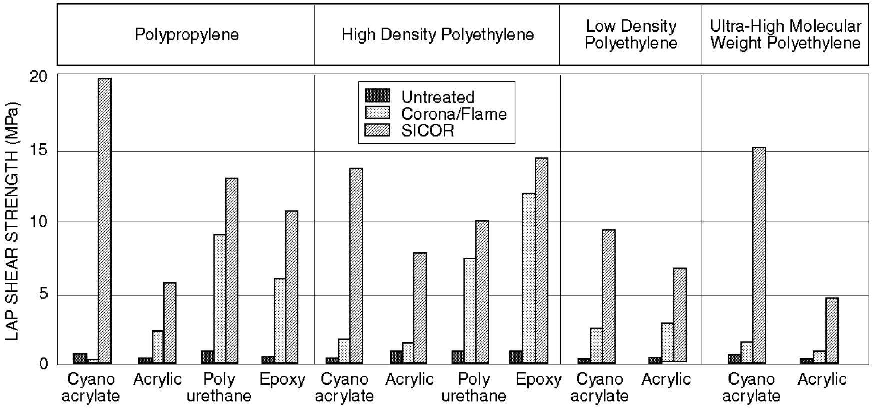


FIGURE 11 Lap-shear strengths of untreated and surface-treated polymeric substrates bonded with a cyanoacrylate (Loctite 406), an acrylic (F241), an epoxy (Araldite 138), and a polyurethane (Tyrite 7520) adhesive [7].

All surface-grafted polymers illustrated in Figure 11, which were bonded with a cyanoacrylate adhesive, exhibited 100% cohesive failure within the substrate. Those specimens, that were surface-grafted and bonded with an acrylic, epoxy, and polyurethane adhesive, exhibited 100% cohesive failure within the adhesive.

In contrast to the above, all untreated and corona discharge-treated specimens exhibited fracture surfaces characterized by 100% delamination between the substrate and adhesive.

The above observations confirm that amino-silane connector molecules grafted onto surfaces of LDPE, PP, HDPE, and UHMW-PE provided an effective multiple "molecular bridge" between the substrates and adhesives investigated in this work, which is capable of withstanding stresses at the interphase equivalent to the cohesive strength of the bonded polymer or that of the adhesive used for bonding.

The advantages of the chemically-reactive connector molecules grafted through the SICOR process are even more obvious when bonded specimens are exposed to wet conditions, as assessed by determining the lap-shear strength of the specimens after immersion for one week and one month in hot water (60°C) prior to testing. Figure 12 illustrates these results for bonds with amino-silane surface-grafted LDPE. The specimens comprising corona-treated LDPE lack resistance to water immersion and delaminate within 1 h. The strength retention of the adhesive bonds comprising NH_3 plasma-treated specimens after one month of hot water immersion is about 60%. The analysis of fracture surfaces subsequent to testing of bonded, NH_3 plasma-modified specimens has revealed that 50% delamination between the substrate surface and adhesive is observed on these specimens. In contrast to the above, no interfacial delamination has been observed in the joints made from the LDPE surface grafted with amino-terminated connector molecules (Z-6020 silane), with 100% cohesive failure within the substrate achieved in this case. The small decrease in the bonded assembly strength may be associated with some plasticizing effect of hot water on the LDPE substrate after prolonged immersion, *i.e.*, one month at 60°C.

Surface-Grafted Connector Molecules Bonding Through the Interpenetration into Adjacent Adhesives

General comments on the scope and limitations of the study. In all experiments discussed in this and the following two sections, the mechanism and effectiveness of adhesion enhancement by surface-grafted connector molecules interacting with self-adhesive pressure-sensitive tape adhesives and crosslinked elastomeric silicone

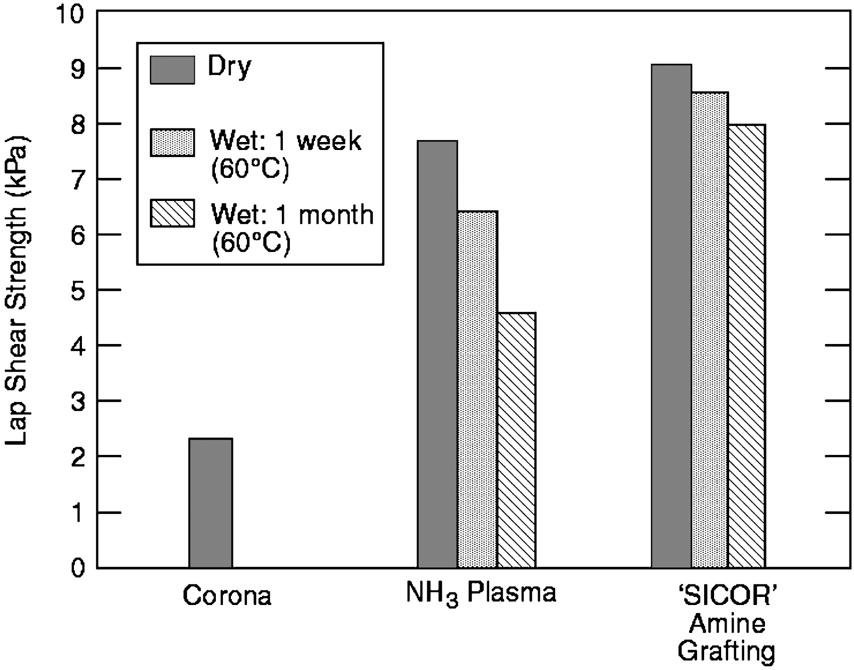


FIGURE 12 Lap-shear strength of LDPE/cyanoacrylate joints in dry and wet environments [7]. Note that wet adhesion was assessed after one week and one-month immersion in 60°C water.

adhesives were investigated using the systems comprising the following materials:

- substrate: PP homopolymer
- pressure-sensitive adhesive tape: VHB 4959/3M (acrylic PSA)
- silicone adhesives: Silbione 70004/Rhone Poulenc
- connector molecules: PEIs: MW = 800 ($N = 19$); MW = 1300 ($N = 46$); MW = 25,000 ($N = 581$); MW = 750,000 ($N = 17{,}442$), and amino-functional silane: Z-6020.

Note that the adhesive in 3M's VHB tape 4959 is thought to be a partially cross-linked acrylic polymer performing a dual role—the foam carrier and the adhesive in one monolithic structure of the self-adhesive tape.

The strength of adhesion was assessed by peel tests using the specimens and procedure described in the section "Peel Specimens, Peel Strength, and Fracture Energy Determination," above. The interface/interphase systems assessed involved PP substrates untreated and surface-treated with corona discharge, and those surface-grafted with connector molecules using the SICOR process.

The molecular bridges were formed by surface-grafting polyethylene imine or silane connector molecules. This was achieved by reacting graft chemicals with the substrate surface for a controlled length of time (30 s) by exposing its surface to water-based solutions of chemicals at the following concentrations: $10^{-5}\%$, $10^{-4}\%$, $10^{-3}\%$, $10^{-2}\%$, 0.1%, 0.5%, and 2%.

Immediately after the reaction, the surface was rinsed with a copious volume of water in order to remove any physically-adsorbed, unreacted chemical molecules from the substrate surface.

Subsequent to surface grafting and peel specimen preparation, the specimens involving the PSA adhesive were conditioned prior to testing at the following conditions: (1) 2 days at 20°C, and (2) 12 h at 60°C in order to provide favourable conditions for enhancing interdigitation of surface-grafted connector molecules into the matrix of pressure-sensitive adhesive.

We infer, without being able to experimentally determine directly, that for a given degree of surface oxidation, the surface density, σ, of graft molecules in the domain of chain density lower than that resulting in the maximum interface reinforcement ($\sigma<\sigma_{\mathrm{OPT}}$) will be directly proportional to the concentration of graft chemical. For concentrations greater than σ_{OPT}, clustering will commence, as discussed in and illustrated in Figure 17 in Gutowski [9], followed by the formation of a continuous film of graft chemical at yet a greater level of concentration of graft chemicals in the carrier solution. The increasing molecular weight of connector molecules will also result in increasing the thickness of the surface-grafted layer.

Interphases interacting with silicone elastomeric adhesives. The mechanism and effectiveness of adhesion enhancement by surface-grafted connector molecules interacting with elastomeric silicone adhesives was investigated using the systems comprising the following materials:

- substrate: EVA(Ethylene vinyl acetate)/PP blend
- silicone adhesive: Silbione 70004/Rhone-Poulenc
- molecular brush: PEI's: MW = 800 ($N = 19$); MW = 2000 ($N = 46$); MW = 25,000 ($N = 581$); MW = 750,000 (N = 17,442), and aminosilane: Z = 6020.

The quality of adhesion was assessed by single lap-shear tests involving the substrates, untreated and surface-treated with corona discharge, and those surface grafted with the following connector molecules: polyethylene imines, as specified above, and an amino-functional silane, Z-6020, at a concentration of 0.1%.

In another experiment, PEIs exhibiting MW = 25,000 and MW = 750,000 were used at concentrations of 0.5% and 1.0%.

Lap-shear specimens were prepared in accordance with procedure described in the section "Lap-shear Specimens and Shear Strength Determination," above. The overlap used was 10 mm. Prior to testing, the adhesive in bonded specimens was allowed to cure for 3 days. Consequently, the specimens were tested in the dry condition, and after 7 days immersion in 40°C water.

Graphs in Figure 13 illustrate the influence of the type and concentration of graft molecules on the strength of assemblies bonded with Silbione 70004 silicone adhesive.

It is seen from the graphs in Figure 13 that the strength of bonded assemblies with specimens surface engineered with molecular brushes provided by surface-grafted polyethylene imine connector molecules, is always greater than that after oxidative treatment such as corona discharge treatment.

A "bare" interface of an oxidised polymer provides the "dry" strength of 180 kPa. Upon 7 days of exposure to 40°C water the bonds between this substrate and silicone adhesives are cleaved, resulting in the loss of strength and complete/spontaneous delamination of adhesive at the interface. An interesting trend is observed regarding the influence of the length of connector molecules on the strength of adhesion. Subsequent to grafting of interpenetrating-only, nonreactive connector molecules of polyethylene imine, increasing the length of graft chemical molecules results in a monotonic increase of the strength of bond, up to approximately 500 kPa achieved by molecules exhibiting the degree of polymerisation of $N = 17{,}442$ at the surface density of chains relevant to a graft chemical concentration of 0.1%. The exposure of this interface to 7 days immersion in 40°C water results in a 35% loss of strength. An increase of surface density of chains, as achieved by the use of a higher concentration of graft chemicals (0.5% and 1%) characterised by degree of polymerisation of $N = 581$ and 17,442, leads to a significant increase of the bond strength (640 and 660 kPa, respectively, for $N = 17{,}442$). Despite significant increase of the strength of adhesion, the failure mode is believed to be interfacial delamination due to the pullout of interdigitating molecular chains from the matrix of the silicone elastomer.

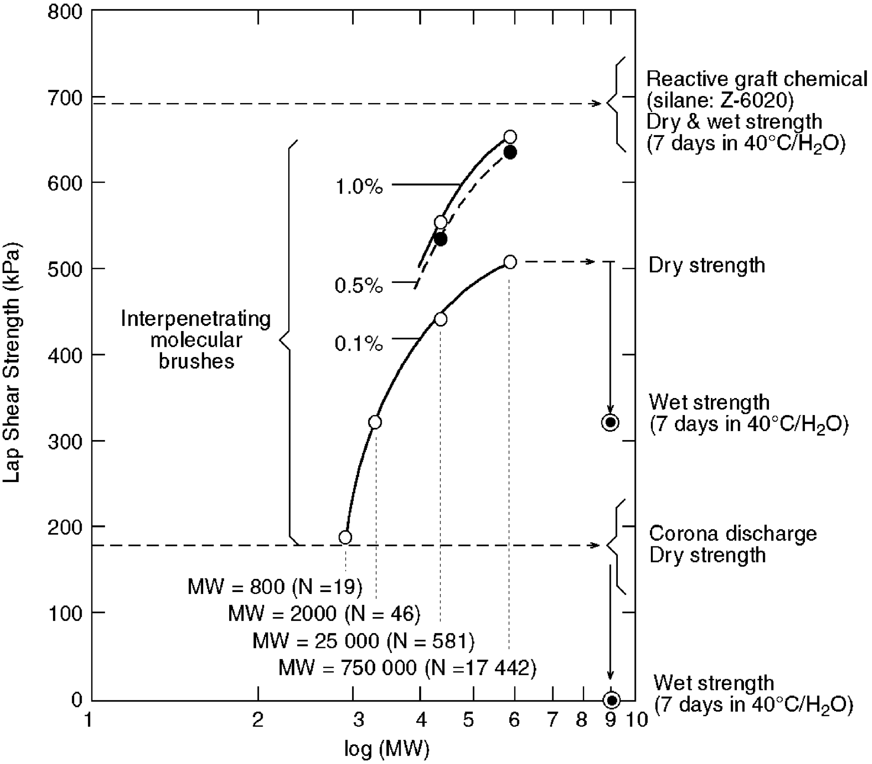


FIGURE 13 The influence of the type of graft chemical: polyethylene imines of various molecular weights (corresponding to varying length of connector chains: $L \propto N$) and amino-silane Z-6020 on the strength of assemblies involving surface-grafted substrate and Silbione 70004 silicone adhesive.

When grafted connector molecules are chemically reactive with the adhesive, which is achieved by the use of amino-functional silane (Z-6020), the highest degree of interphase reinforcement is achieved: up to the level of 690 kPa. This particular interface/interphase system involving chemically bonded connector molecules retains the strength of the bond at the original level of 690 kPa subsequent to 7 day immersion in 40°C water.

Interphases interacting with elastomeric pressure-sensitive adhesives. 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 systems comprising the following materials:

- substrate: PP homopolymer
- pressure-sensitive adhesive tape: VHB 4959/3M (acrylic PSA)
- connector molecules: PEIs: MW = 800 ($N = 19$); MW = 1300 ($N = 46$); MW = 25,000 ($N = 581$); MW = 750,000 ($N = 17{,}442$).

The quality of adhesion was assessed by peel tests using the specimens and procedure described in section "Peel Specimens, Peel Strength, and Fracture Energy Determination," above. The interface/interphase systems assessed involved PP substrates untreated and surface-treated with corona discharge, and those surface grafted with connector molecules using the SICOR process. The molecular brush was formed by surface-grafting polyethylene imine connector molecules applied from water-based solution at the following concentrations: 10^{-5}%, 10^{-4}%, 10^{-3}%, 10^{-2}%, 0.1%, 0.5%, and 2%.

Subsequent to surface grafting and peel specimen preparation, the specimens were conditioned prior to testing at the following conditions: (1) 2 days at temperature of 20°C, and (2) 12 h 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 the interactions present in the experiments illustrated in Figures 14–17 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.

The graphs in Figures 14 and 15 illustrate the behaviour of graft chemicals adsorbed from solution of the carrier liquid at varying concentrations and then chemically bonded to the surface of oxidised substrate. According to the theories discussed in Gutowski [9], the most favourable conditions for the provision of maximised adhesion exist when single macromolecular chains, appropriately separated, are grafted at the polymer surface (see Figure 17 in Gutowski [9]). The increase of concentration above the optimum leads to clustering of entangled multiple chains up to the point where an 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 presented in Figures 14 and 15 that, in accordance with the discussion presented in Gutowski [9], for all lengths of connector chains of molecules (N) used in our experiments there is a distinct optimum (σ_{OPT}) in the surface density (σ) of connector molecules which has to be achieved in order to maximise the adhesion between a surface-modified substrate and the adjacent

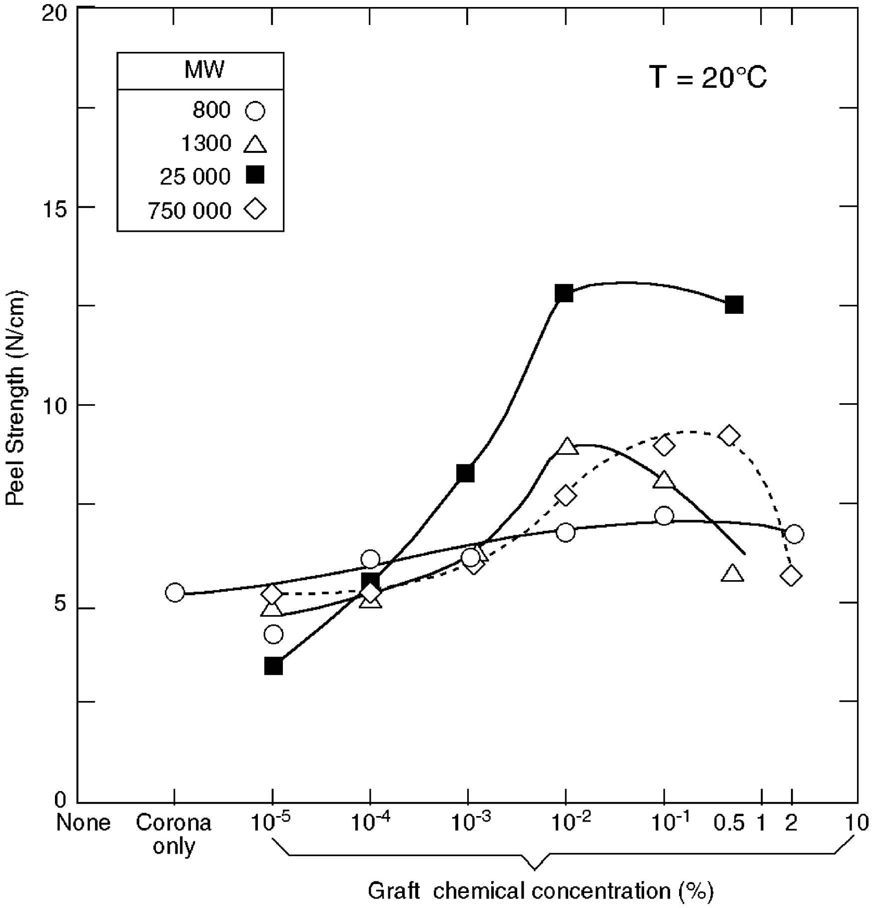


FIGURE 14 The influence of the length of PEI connector molecules ($L \propto M$; $L \propto N$) surface grafted onto PP substrate at various concentrations in carrier solution (water) on the peel strength of connector-chains reinforced interface bonded with elastomeric pressure-sensitive adhesive (4959/3M); temperature: 20°C.

polymeric material, such as the matrix of the cross-linked pressure-sensitive adhesive.

As theoretically determined by de Gennes [18, 19], Léger *et al.* [20], and Brochard–Wyart [21], and confirmed by our results illustrated in Figures 14 and 15, 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

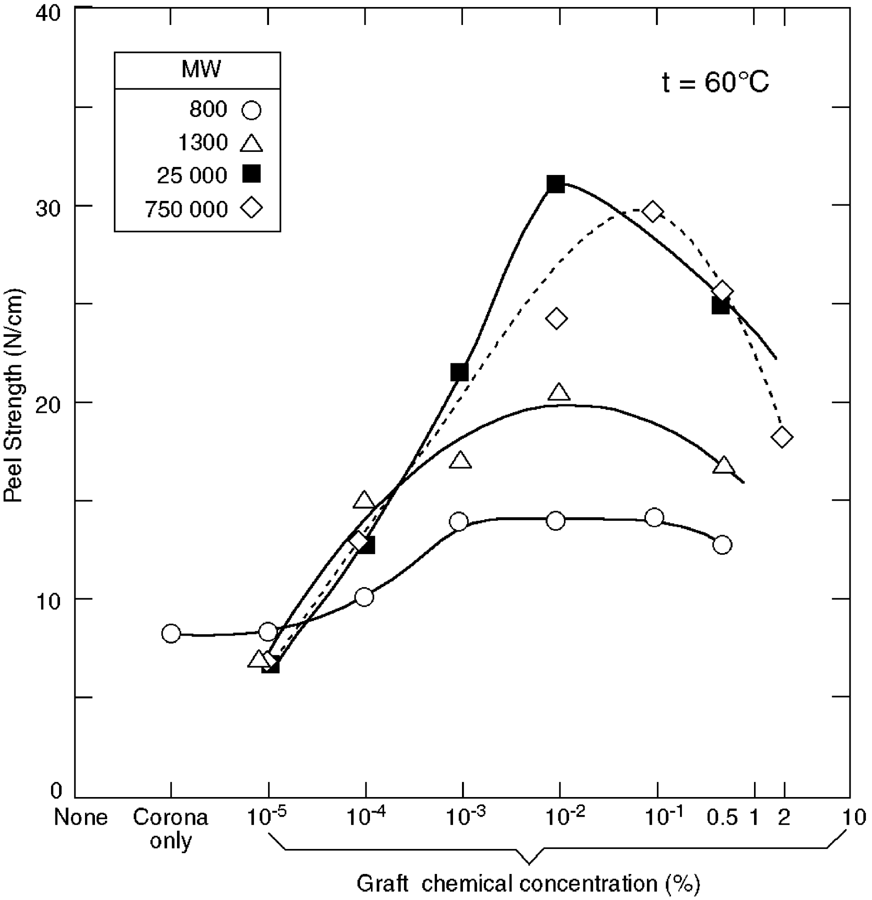


FIGURE 15 The influence of the length of PEI connector molecules ($L \propto M$; $L \propto N$) surface grafted onto PP substrate at various concentrations in corner solution (water) on the peel strength of connector-chains reinforced interface bonded with elastomeric pressure-sensitive adhesive (4959/3M); temperature: 60°C.

adjacent polymer. This is in good qualitative agreement with Equation (17) in Gutowski [9].

Another noticeable feature of Figures 14 and 15 is the significant increase of peel strength for 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 cross-linked pressure-sensitive adhesive constitutes an important part of the enhancement of adhesion by surface-grafted connector

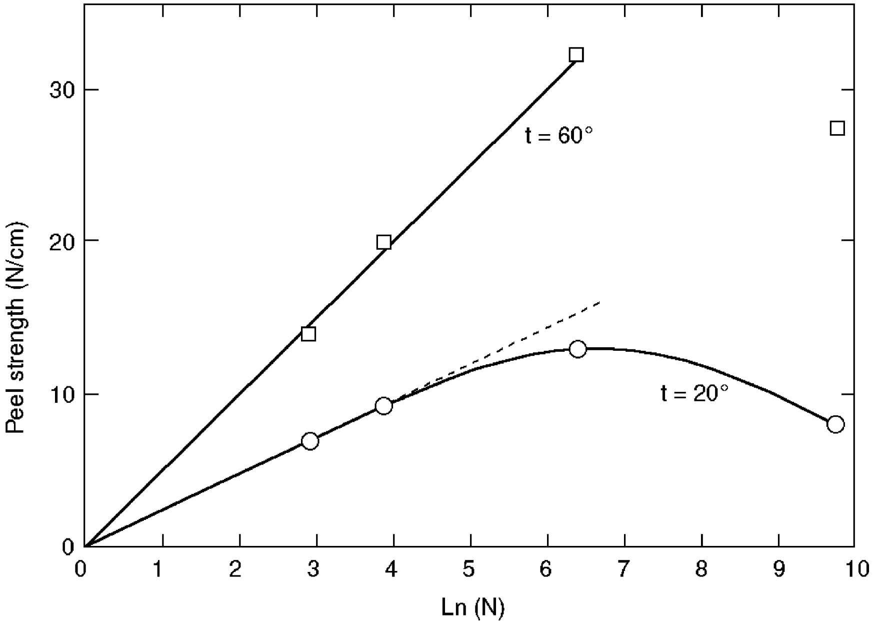


FIGURE 16 The relationship between the length of connector molecules ($L \propto N$) surface grafted onto PP substrate at 0.01% concentration, and the peel strength of the interface between surface-grafted PP and elastomeric pressure-sensitive adhesive (4959/3M). Note the following features of the graphs: (i) Nearly linear increase of the bond strength for connector molecules representing $N = 19$ to $N = 581$, and (ii) Significant interface reinforcement of specimens conditioned at 60°C to facilitate deeper penetration of surface-grafted connector chains into the matrix of pressure-sensitive adhesive, in comparison with those conditioned at 20°C.

molecules. Interpenetration of grafted PEI molecules into the pressure sensitive adhesive tape (PSA) can be promoted by the effect of heating and hence improve the interface interactions resulting in an increase of bonding strength as observed.

According to the theoretical models of de Gennes [18, 19], Léger *et al.* [20], and Brochard–Wyart [21], once the surface density of grafted macromolecular chains starts to exceed that corresponding to the optimum concentration of graft chemical in the carrier solution (and consequently the corresponding (σ_{OPT}) only partial penetration into the adjacent adhesive or matrix occurs. It may be considered that the following might be simultaneously occurring under these circumstances: (a) only a fraction of grafted chains fully penetrate into the adjacent polymer; (b) fractional length penetration of some chains occurs; and

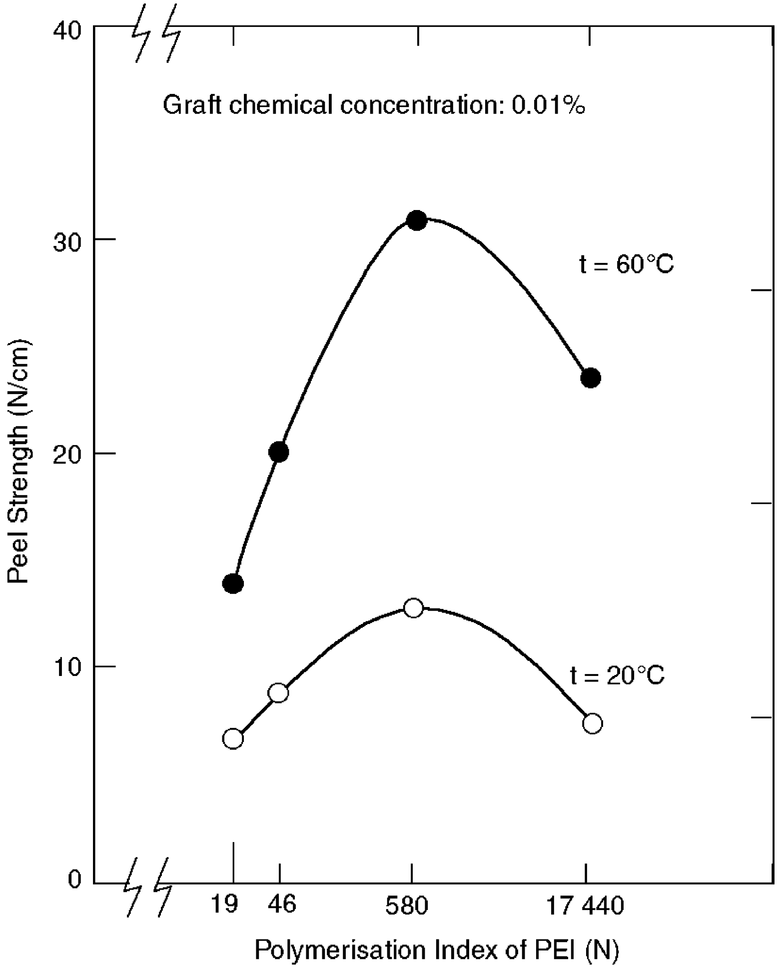


FIGURE 17 The relationship between the length of PEI ($L \propto N$) connector molecules surface-grafted onto PP substrate at the constant concentration of 0.01% on the peel strength of the interface between surface-grafted PP and elastomeric pressure-sensitive adhesive (4959/3M).

(c) the network of the adjacent polymer may reject some chain ends. This, consequently, leads to the gradual decrease of bond strength or fracture energy to the level equal to that of an unmodified substrate when the concentration of graft chemical and the corresponding surface density of chains, (σ), exceeds the σ_{OPT} relevant to the optimum concentration of given graft chemicals used in our experiments.

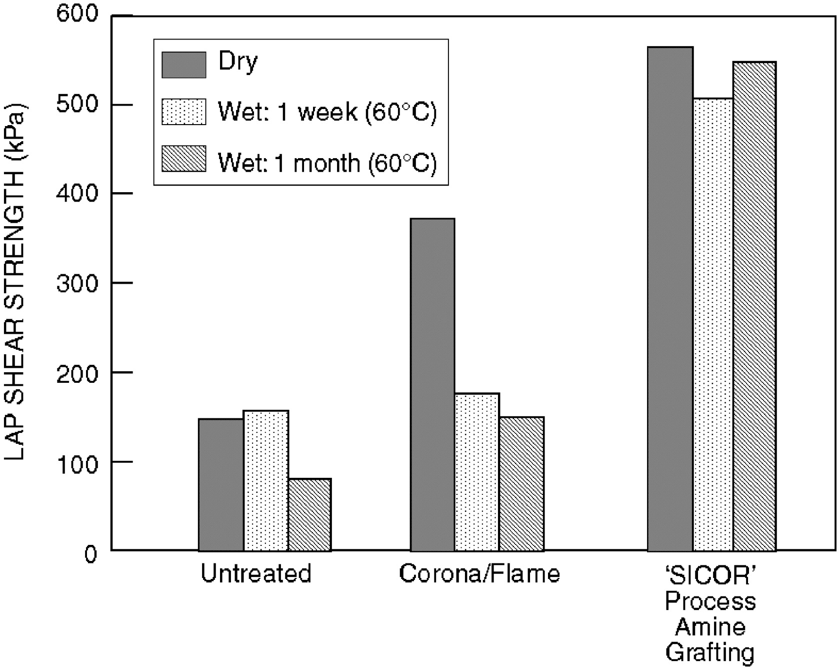


FIGURE 18 Lap-shear strength of PP homopolymer, untreated and surface modified by corona or flame treatment and surface grafted with macromolecular connector molecules (flame oxidation + 0.25% PEI ($M_w = 750{,}000$)) for improved adhesion of PSA tapes [7].

Our experiments illustrated by the data represented in Figures 14 and 15 confirm the above theoretical predictions concerning the profile of the relationship between the strength of the interface *versus* the surface density of surface-grafted macromolecular chains (see discussion in Gutowski [9]) regarding van der Waals interactions of interdigitated connector molecules with the adjacent elastomeric adhesive/polymer).

It was also visually observed in our experiments that at the optimum grafting conditions, i.e., $N = 581$ and 17,442, concentration between 0.01 to 0.1% and conditioning at 60°C for 12 h, partial cohesive failure within the elastomeric pressure sensitive adhesive is achieved. While the locus of failure is clear for these areas, the locus of failure for other concentrations of graft chemicals (corresponding to the area below and above σ_{OPT}) is not yet clear due to the absence of visually observable cohesive failure within the adhesive layer in peeled-off specimens.

Surface analysis by XPS on the debonded interfaces was recently carried out, using the specimens from our original experiments that had been stored for a period of approximately 12 months. The quantitative results given below are, therefore, indicative only, due to the fact that the prolonged storage of the specimens may have led to the reorientation of molecular chains on the PP substrate and in particular on the pressure-sensitive adhesive surface. Consequently, the chemical compositions obtained may not represent the surfaces immediately after delamination of the specimens.

For the specimens grafted with PEI molecules of $N = 17{,}442$ and at concentrations varying from 0.01 to 2%, Nitrogen was found on both surfaces. About 2% to 2.5% of amine (nitrogen) was detected on the PP surface, and the amount of amine increased with the increase of concentration of the graft chemical in solution. It was also observed that approximately 15% to 20% of equivalent amine was detected on the matching PSA surface. The total amine content found on both sides is equal, however, to only about half of the amine originally introduced on the PP surface (before the PP and PSA were bonded together). As amine is not present on the original PSA surface, the presence of amine on both surfaces of the delaminated specimens could indicate either or both of the following: (1) some chain scission of PEI connector molecules taking place during the interface fracture, or (2) interdiffusion of PEI originally on the PP surface to the PSA surface and sub-surface layer. A systematic study on the surfaces of freshly peeled specimens is currently being carried out and the findings will be published in a separate paper.

Another significant observation from the graphs in Figures 14 and 15 points to the fact that the length of connector molecules, as relevant to their molecular weight (or corresponding to the degree of polymerisation, N) for the range of $N = 18.6$ to 17,440, has a significant influence on the maximum achievable peel strength (and corresponding fracture energy: see Equation, (3)) of the interface/interphase system. Particularly significant information is gained from the graphs in Figure 16, which show that an almost linear increase of the peel strength *versus* N is observed for the length of connector chains in the range of $N = 19$ to 581. This finding confirms that the chain pullout appears to be the main mechanism of interface failure in this region, in agreement with the theoretical models of Xu *et al.* [22] and de Gennes [18].

Figure 17 represents 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 temperatures 20°C and 60°C from Figures 14 and 15.

It is clear from the graphs in this figure that a well-pronounced optimum in the interface reinforcement by surface grafted connector chains occurs at the length of $N = 580$.

An identical trend has been observed by Norton *et al.* [17] in their work on the explanation of the mechanism of interfacial interactions between PS and epoxy surface-grafted with deuterated PS-COOH graft molecules. Norton *et al.* findings are illustrated in Figure 9b in Gutowski [9]. The decrease of the interface-reinforcing efficiency of connector molecules (dPS-COOH) exhibiting the chain length greater than the optimum ($N_{OPT} \cong 840-1000$ in Norton *et al.* experiments) is attributed to the significant decrease of the effective number of graft molecule chains (σ = surface density [chains/nm^2]) per surface area. It has been shown by Norton *et al.* (see Figure 9a in Gutowski [9]) that, for their systems involving PS-COOH, there is a nearly linear decrease in σ (chains/nm^2) with the increase of the length ($L \propto N$) of connector molecule chains.

The above phenomenon can be attributed to the effect of an entropic barrier to grafting that opposes 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/nm^2), 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 ($\sigma < \sigma_{\mathrm{OPT}}$), 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, as discussed in Gutowski [9] and illustrated in Figure 17 in Gutowski [9].

Another set of results (Figure 18) demonstrates the outcome of experiments on the bonding of PP homopolymer, surface-grafted with molecular brushes, using VHB pressure sensitive adhesive tape 4959 3M in lap-shear mode.

Figure 18 compares the effectiveness of adhesive bonding of PP surface-modified by molecular brushes achieved through surface grafting (SICOR process) of poly-functional amino-compound (PEI: $M_w = 750{,}000$) with that involving PP substrates, either untreated or surface-oxidised by flame or corona treatment. It is seen from Figure 18 that the performance of specimens involving connector molecules is superior to those using untreated or oxidised PP. The performance of the bonded assembly involving surface-grafted connector molecules in this instance is limited only by the cohesive strength of the tape, with 100% cohesive failure within the tape; flame and corona oxidation both demonstrated 100% interfacial delamination failure between the pressure-sensitive adhesive tape and polypropylene.

The molecular chains of graft chemical are thought to be able to interpenetrate the elastomeric matrix of the partially cross-linked PSA to a sufficient depth, thus resulting in enhanced performance of the interphase up to a level sufficient for creating 100% cohesive failure within the adhesive, in the "lap-shear" configuration of the test specimen.

CONCLUSIONS

1. The surface grafting of chemically reactive or interpenetrating connector molecules (SICOR process) comprising surface oxidation and the deposition of polyfunctional connector molecules, as discussed in this paper, provides a very effective means for enhancing adhesion of polymers to a range of typical engineering adhesives, elastomeric sealants, organic coatings and other materials. Cohesive failure within the substrate, or adjacent material (*e.g.*, adhesive, sealant, or coating) can be achieved at optimum process conditions.
2. A comparative study of SICOR with other surface modification processes for polymers such as flame, corona, or plasma treatment indicates that the SICOR process based on the principles of chemically reactive or interpenetrating connector molecules offers the following key advantages over other current surface treatment technologies:

    - It provides significantly enhanced bond adhesion strength and durability when compared with current methods of polymeric substrate treatment.
    - It provides significant cost savings when compared with all currently known competitive surface treatment processes, such as plasma treatment or primers, by allowing the use of cheaper commodity chemicals and processing equipment.
    - The process can be easily integrated into existing manufacturing systems, treating at speeds up to and in excess of 85 m/minute.
3. The technology developed and analysed in this work has been extensively tested and validated for a range of manufacturing applications, demonstrating excellent results on normally difficult-

to-bond homopolymers and blends based on polyethylene, polypropylene, and other plastics.

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