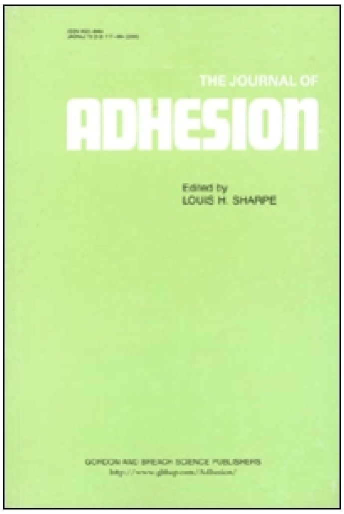

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface Silanization of Polyethylene for Enhanced Adhesion

W. S. Gutowski[a,b]; D. Y. Wu[a,b]; S. Li[a,b]
[a] CSIRO Division of Building, Construction and Engineering, Melbourne, Australia [b] CSIRO Division of Building, Construction and Engineering, Highett, Victoria, Australia

To cite this Article Gutowski, W. S. , Wu, D. Y. and Li, S.(1993) 'Surface Silanization of Polyethylene for Enhanced Adhesion', The Journal of Adhesion, 43: 1, 139 — 155

To link to this Article: DOI: 10.1080/00218469308026593

URL: http://dx.doi.org/10.1080/00218469308026593

J. Adhesion, 1993, Vol. 43, pp. 139–155
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Surface Silanization of Polyethylene for Enhanced Adhesion

W. S. GUTOWSKI, D. Y. WU and S. LI

CSIRO Division of Building, Construction and Engineering, Melbourne, Australia
Postal Address: PO Box 56, Highett, Victoria, 3190, Australia

(Received September 9, 1992; in final form July 13, 1993)

Low density polyethylene has been treated using a novel surface treatment process "SICOR" ("**SI**lane-on-**COR**ona" treated polymer) in order to enhance adhesion with a range of adhesives including polyurethane, methacrylate and cyanoacrylate. The process comprises two steps, *i.e.* corona discharge followed by application of an organo-functional silane. The incorporation of surface hydroxyl groups onto the polymer surface enables organo-silane to create the hydrogen or covalent bonds with the oxidized polymer surface. The possibility of the creation of these bonds has been investigated using FTIR, XPS and wettability studies. The adhesion enhancement due to the new process is significant. Frequently, the strength increase exceeds 200% compared with the corona discharge treatment and more than 300% compared with LDPE priming using the "Loctite 770" polyolefin primer. The process is shown to be as good as, or better than, plasma treatment in terms of the strength increase following substrate treatment prior to adhesive bonding.

KEY WORDS polyethylene; corona discharge; plasma; polymer surface silanization; silanes; adhesive bonding.

INTRODUCTION

Polyolefins, such as polyethylene and polypropylene, are attractive for various engineering and manufacturing applications due to their low cost, easy processability, low vapour transmission, high impact resistance and other qualities. As saturated hydrocarbons, however, they exhibit very low polarity and thus very poor affinity to adhesives, paints, and printing inks which frequently limits their applications. Numerous surface pre-treatments of polyethylene are known to improve its bonding ability. Most of these processes are oxidative in nature and they include the chemical,[1-8] flame,[9-10] corona discharge and plasma treatments.[11-14]

The incorporation of oxygenated chemical species such as hydroxyl, ether and carbonyl onto the surface of polyethylene is generally sufficient in providing a surface receptive enough for selected adhesives or paints. However, it is frequently required to engineer the surface properties of a polymer to optimise its performance further from the viewpoint of the most preferable interactions occurring across the substrate/adhesive or substrate/paint interface. Plasma treatment is a commonly-used process for this purpose. This process allows 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 typically associated with the need for vacuum equipment. Also, in most cases plasma treatment can only be used for batch processing. Although continuous plasma treatment equipment is known and is described in the literature,[15–17] its technological applications are limited.

A new surface treatment technique for enhancing adhesion of polymers, whose effectiveness is shown to be similar to that of plasma, has been developed by CSIRO.[18–21] The process adopts the concept of use of various coupling agents as adhesion promoters, *e.g.* organo-silanes, to modify the properties of polymers in a manner similar to that already known in controlling and enhancing adhesive properties of metals or oxide-based ceramics *e.g.* glass fibres, etc. In a number of cases, untreated polymeric materials are not receptive to silanes in terms of hydrogen or covalent bonding capability due to the absence of the required surface chemical functionalities. This can be overcome by an oxidative treatment of the polymer surface in order to provide appropriate sites, *e.g.* OH, C=O, COOH, etc. capable of chemically interacting with silanes. Thus, the new surface treatment for polymeric materials, SICOR (silane-corona) comprises two following steps:

(a) surface oxidative treatment by a physical and/or physico-chemical means, *e.g.* corona discharge or flame treatment, followed by
(b) application of a silane or other adhesion promoter equipped with the atomic species/molecules capable of creating hydrogen, or covalent, bonds with the oxygenated surface species.

A similar principle, applied for adhesion enhancement of ultra-high modulus polyethylene (UHMPE) fibres to epoxy matrix, has been reported by Choe and Jang,[22] who suggest application of oxygen plasma in order to incorporate hydroxyl groups onto the fibre surface prior to further silanization.

Two recently-published papers report additional improvement of adhesive properties of poly(p-phenylene terephthalamide (PPTA) fibres to silicone rubber after an initial plasma treatment,[23] and silanization of PTFE[24] with amino-silanes.

The effectiveness of the new surface treatment process, SICOR, is analysed in this paper in terms of surface chemistry and bondability of an untreated and modified polymer. The surface properties of substrates and performance of adhesive bonds are compared with those apparent after corona discharge and plasma treatment. The surface chemistry is studied by the use of FTIR, XPS and wettability studies. The adhesion enhancement is assessed by using three generic types of adhesives *viz:* polyurethane, methacrylate and cyanoacrylate.

EXPERIMENTAL

Materials

A 150 μm thick low density polyethylene (LDPE) film was used for contact angle and FTIR measurements. Sheets of 1.5 mm thick LDPE were used for adhesive bonding experiments discussed in this paper. Prior to use, all samples were immersed in ethanol overnight to remove additives and surface impurities introduced during processing and handling. Samples were then dried in an oven at 40°C for 4 h.

A silane coupling agent, N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (Z-6020) (γ-APS) was obtained from Dow Corning and used after preparation described below.

Three commercially available adhesives were used:

(a) a two-part polyurethane adhesive: "Tyrite 7520" from Lord Industrial Adhesives,
(b) a two-part acrylic paste adhesive: "F241" from Permabond Ltd,
(c) one-part cyanoacrylate: "406" from Loctite International.

Methods

Corona discharge treatment All corona discharge experiments were carried out in ambient air, with a Tantec® (Tantec EST) corona generator, model HV 05-02, with adjustable power output (6 to 350 W), equipped with the high-frequency generator (20–30 kHz) and high-power transformer providing high voltage in the range of 21–28 kV. The speed of the treatment table carrying the sample could be adjusted continuously within the range of 1.2 to 70 mm/s. The distance between the polymer surface and the electrode was fixed at 2.5 mm in this work. The relative humidity was 55–65%.

The discharge energy supplied to the substrate interface was determined by

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

where P = power output [watts],
t = time required to treat the substrate length unit under the electrode of a diameter, d, in mm [time = d/V; where V = table velocity in mm/s],
n = number of table passes under the electrode.

The energy output, E_u, per unit of the substrate surface area is

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

where L is the length of the treating electrode in mm.

Silane preparation and application γ-APS was first hydrolysed with distilled water at 1:3 (silane/water) mole ratio for 24 h. The hydrolysed silanes were then diluted with isopropanol to obtain 0.05 to 1% solutions.

The LDPE sheets, untreated or treated by corona discharge, were immersed in silane solution for 30 s, after which the samples were dried in air for 30 min, followed by drying in an oven at 40°C for 4 h. After initial experiments, an oven drying step was abandoned since no significant difference was observed between the air-dried and oven-dried specimens.

Plasma treatment For comparative purpose, the samples of LDPE were also submitted to plasma treatment, which was carried out in the laboratories of CSIRO Division of Chemicals and Polymers, Melbourne. Three process gases were used: air, ammonia and heptylamine. A custom-built reactor[25] was used for the plasma treatment. The reactor contains two capacitively coupled, parallel electrodes, which are rectangular in shape and of dimensions 18 by 90 mm. Plasma treatment was driven by a custom-built oscillator operating at 700 kHz, with a power input of 35 W at a pressure of 0.6 Torr. The treatment times were 150 s, 10 min and 20 min.

Contact angle measurement The contact angles of water, diiodomethane and α-bromonaphthalene were determined using the sessile-drop method in a Ramé-Hart contact angle goniometer model 100. Measurements were performed in a chamber saturated with the vapour of the test liquid. The equilibrium contact angle was measured after allowing fifteen minutes to elapse from the application of the drop, and averages were calculated using values obtained from at least five separate droplets. Observed angles usually agreed within ±2° for a given surface.

FTIR analysis A Fourier transform infrared spectrophotometer, BIO-RAD FTS-7R1, 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 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 minimise 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 polymer sample were obtained by co-adding 64 scans.

XPS analysis The XPS analysis was performed using an XPS spectrometer with a Mg Kα source. Survey spectra were obtained at an 80° take-off angle at a pass energy of 50 eV at 300 W. The resolution was 0.05 eV.

Adhesion tests The bond strength of surface-modified PE joints was evaluated by the tensile lap shear tests. These were carried out using a modified ASTM D3163 specimen. The substrate dimensions were 50×25 mm instead of 100×25 mm suggested in the standard. Shorter substrates were chosen for purely economical reasons due to the significant quantity of materials used in our experiments. The size of an overlap was 3 mm instead of the typical 12.7 mm due to the fact that 100% cohesive substrate failures were predominantly achieved with the SICOR-treated LDPE when larger overlaps were used. Prior to test, adhesives were allowed to cure for 3 days at room conditions (21±2°C; RH=50±5%). Testing has been carried out on an Instron mechanical tester at the crosshead rate 10 mm/min under controlled room conditions, 21±2°C and RH=55±5%. Five specimens were tested at each test condition. The typical deviation in the measured bond strength was within 8 to 10% of the reported mean values.

RESULTS AND DISCUSSION

Surface Chemistry of LDPE after Various Types of Surface Treatment

Corona discharge treated LDPE The chemical modification of LDPE after corona treatment was investigated by FTIR-ATR analysis. LDPE samples treated by corona discharge including high (755 mJ/mm^2) and low (8.7 mJ/mm^2) discharge energy levels were examined by FTIR-ATR (Figure 1). From the spectrum of the sample treated by the high energy corona discharge (755 mJ/mm^2), one can see an absorption band in the 3300 cm^{-1} region which is typically assigned to OH hydroxyl groups. Interestingly, the XPS analysis of a corona discharge treated LDPE which is the subject of another paper prepared for publication[31] indicates that a small, but noticeable, quantity of nitrogen has also been incorporated onto the polymer surface. It is, therefore, possible that the broad band at 3300 cm^{-1} can be attributed not only to the stretching vibrations of hydrogen-bonded —OH but also to a mixture

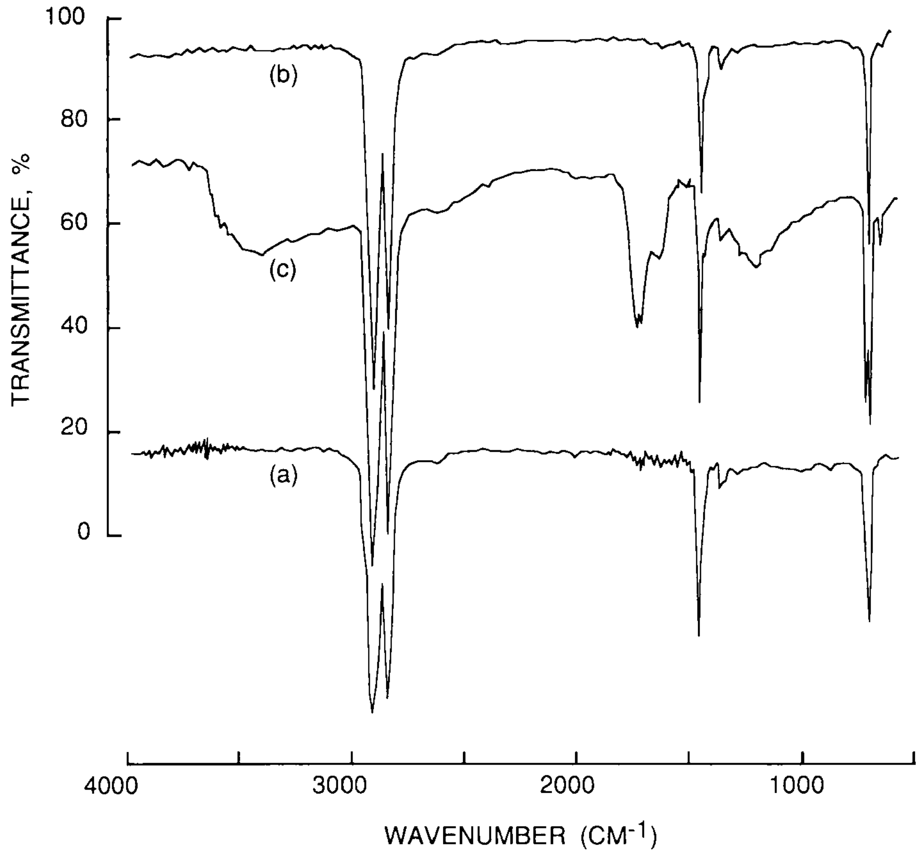

FIGURE 1 FTIR-ATR spectra of LDPE: (a) untreated; (b) corona treated at a low discharge energy level (8.7 mJ/mm^2); (c) corona treated at a high discharge energy level (755 mJ/mm^2).

of NH and NH_2. For the same reason, another band at 1630 cm^{-1} may be assigned to either double bonds (C=C) or amino groups, NH_2. Another peak at 1720 cm^{-1} is characteristic of carbonyl groups (C=O), whilst the absorption band at 1200 cm^{-1} is due to ether functional groups (C—O). However, FTIR-ATR analysis failed to detect any significant change on the surface of the sample treated by the low energy corona discharge (8.7 mJ/mm^2), although the contact angle measurements showed that the polar component of the surface free energy (γ_s^p) of LDPE increased from 0.4 mJ/m^2 for the untreated sample to 13.6 mJ/m^2 for the low energy (8.7 mJ/mm^2) treated sample. This can be explained by the fact that the low energy corona discharge treatment produced a chemical modification in a very thin layer of the polymer surface, which is beyond the sensitivity of detection of the FTIR-ATR technique.

Surface-silanized LDPE The "as received" surfaces of polymers, *e.g.* LDPE, are not receptive to silanes in terms of chemical bonds across the polymer-silane interface due to the absence of appropriate surface chemical groups. It is shown by FTIR study (see Figure 2) that the γ-APS silane adhered to the untreated (*i.e.* "as received") LDPE surface as a physisorbed film that could be removed by a rinse in water or isopropanol.

It is noticeable, however, from spectrum (b) in Figure 2 that there is some residual silane retention after the isopropanol wash, as indicated by a residual absorption

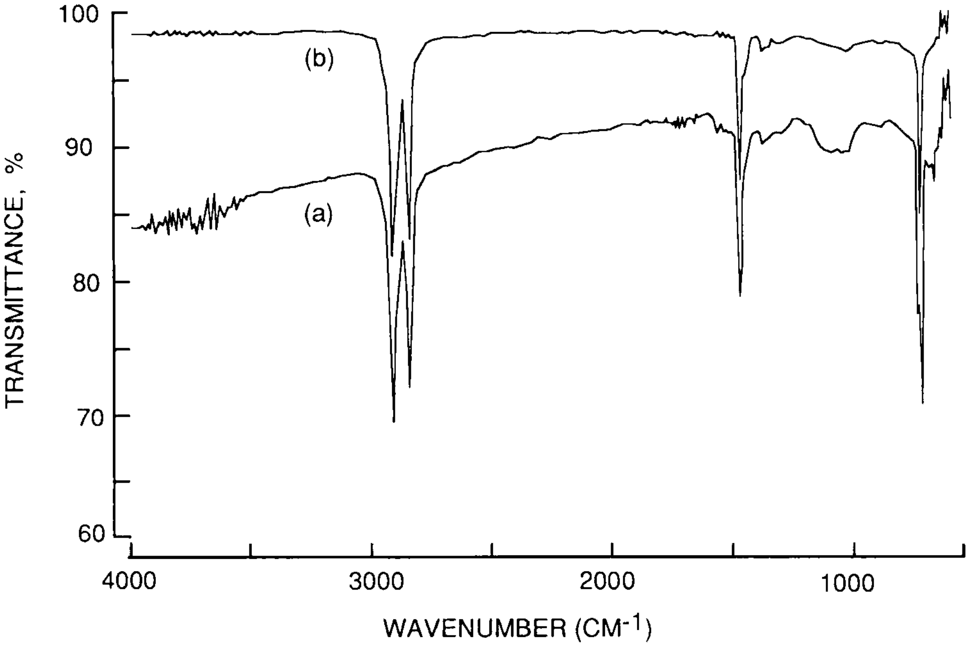

FIGURE 2 FTIR-ATR spectra of LDPE primed with 0.1% solution of γ-APS in isopropyl alcohol without any polymer pre-treatment prior to silane deposition: (a) LDPE with physisorbed γ-APS; (b) the same specimen after rinse with water or isopropanol.

near 1100 cm^{-1} which is characteristic of Si—O—Si bonds. This phenomenon can be explained using results of an XPS analysis which show the presence of a small quantity of oxygen in the spectrum of untreated LDPE (result not shown in this paper). It is likely that some residual quantity of silane is 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 the Instron mechanical tester.

The introduction of surface-oxygenated species after corona discharge or other oxidizing treatment provide receptive sites capable of forming either hydrogen or covalent bonds with the silane molecules. Figure 3 illustrates the FTIR-ATR spectra of LDPE after the "SICOR" silanization process described in this paper. The first of these spectra, (b), was taken from a freshly silanized LDPE whilst the second is that of the same specimen subjected to immersion in isopropanol for 1 week

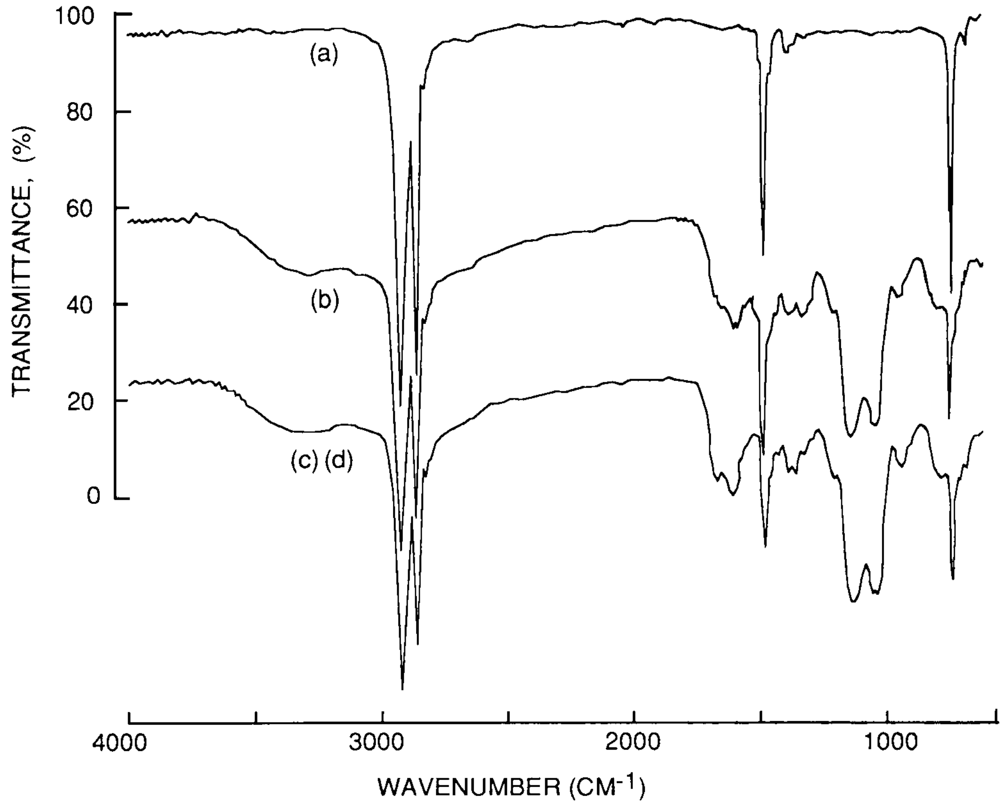

FIGURE 3 FTIR-ATR spectra of LDPE illustrating the performance of γ-APS on LDPE after SICOR silanization: (a) untreated LDPE: (b) SICOR silanization: corona discharge treatment (755 mJ/mm^2) + 0.1% γ-APS; (c) as in (b) after 1 week in isopropanol; (d) as in (b) after 2 months immersion in isopropanol.

[spectrum (c)] and 2 months [spectrum (d)]. It is evident from this illustration that the spectrum of a freshly-silanized surface of LDPE is very similar to that immersed in isopropanol for either 1 week or 2 months. This shows that the silane molecules were bonded firmly to the polymer surface either by chemical or by hydrogen bonding. There is a small, but nevertheless noticeable, difference between the spectra of freshly-silanized and isopropanol-aged surfaces 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. This, however, will be a subject of further study and is beyond the scope of this paper.

Further analysis of the FTIR-ATR spectrum of LDPE silanized through the corona discharge treatment and application of a silane solution warrants several comments. First of all, the broad band appears at 3300 cm^{-1} (Figure 1), which can be assigned to a mixture of OH, NH and NH_2 hydrogen-bonded stretching vibrations. The band at 1590 cm^{-1} is attributed to a mixture of free primary and secondary NH bonds, and the one at 1650 cm^{-1} is assigned to the amine deformation mode of acceptor amine groups involved in strong hydrogen bonding. The absence of the carbonyl absorption band at 1720 cm^{-1} might be explained by the formation of hydrogen bonds between the carbonyl groups on 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. The strong bands at 1130 and 1035 cm^{-1} are characteristic of siloxane (Si—O—Si) polymer. The band at 930 cm^{-1} is assigned to the SiO stretching mode of the silanol.[26]

The spectra of the LDPE treated by corona discharge and silane under the same conditions, but subsequently immersed in water for a period of 1 week and 2 months, are shown in Figure 4. A comparison of the IR spectra of the freshly-silanized material with those obtained after water immersion indicates noticeable changes to the surface chemistry upon prolonged exposure to water (see spectrum (c) and (d)). The major differences between the freshly-silanized LDPE surface (as well as silanized material exposed to isopropanol) and the polymer aged in water can be explained by the displacement by water of some silane, hydrogen-bonded to the oxygenated polymer surface through either —OH groups or NH_2 groups, which were not displaced by less polar isopropanol. This phenomenon is evidenced by 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 hydrolyzed methoxy silane. Another absorption band at 930 cm^{-1} not removed by water immersion is attributed to SiOH.[26] Again, the absence of the carbonyl band at 1720 cm^{-1} originally present in the corona discharge only treated LDPE (see spectrum (c) in Figure 1) together with the presence of the 1650 cm^{-1} band in the IR spectra of the material aged in water after original silanization (Figure 4b, c and d) can be interpreted as the shift of the band from 1720 to 1650 cm^{-1} as a result of the formation of hydrogen bonds between carbonyl groups of the polymer surface and amino and/or hydroxyl groups of the silane molecules. The peak at 1590 cm^{-1},

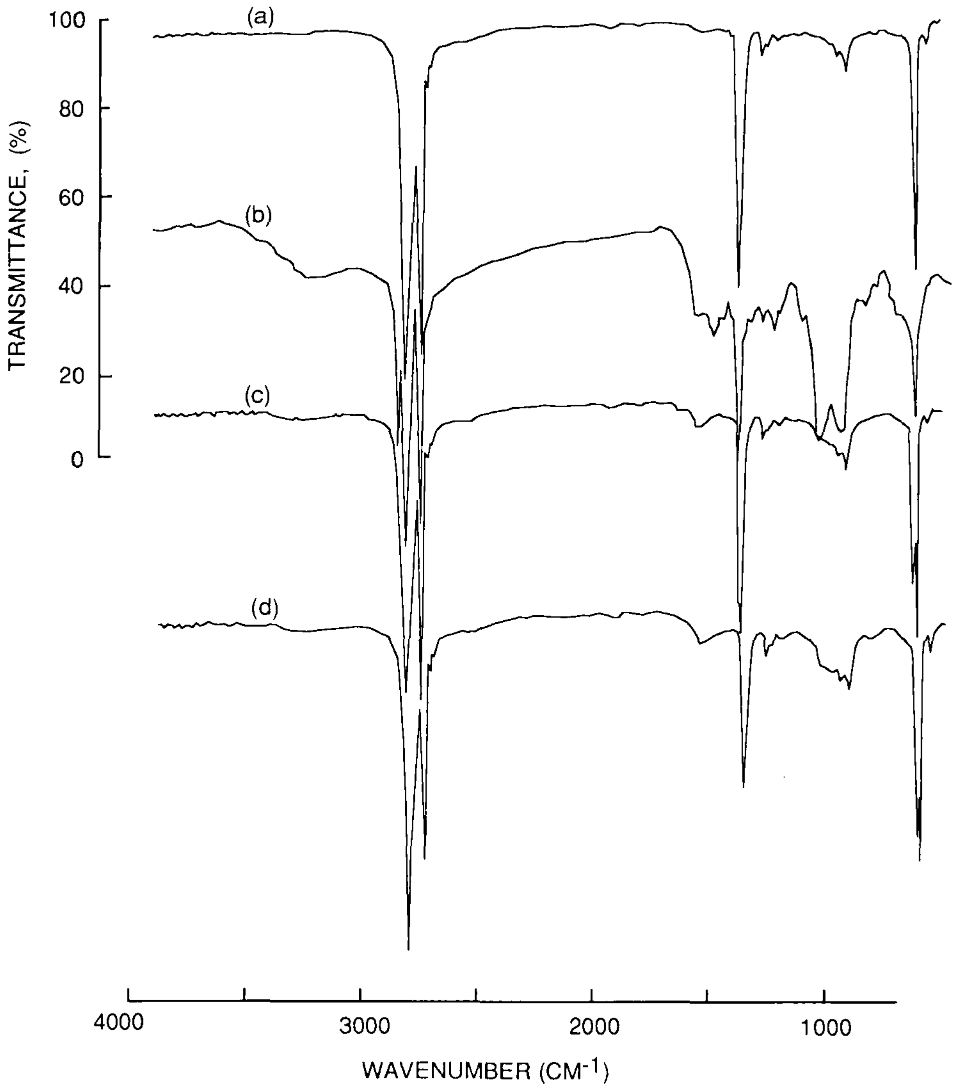

FIGURE 4 FTIR-ATR spectra of the γ-APS silanized LDPE after immersion in water: (a) untreated LDPE; (b) SICOR silanization: corona discharge treatment (755 mJ/mm^2) + 0.1% γ-APS, (c) as in (b) after one week immersion in water; (d) as in (b) after 2 months immersion in water.

which is due 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. From the above observations, it seems that the silane layers on the surface of corona discharge oxidized and silanized LDPE contained both physisorbed and chemisorbed silane coupling agent. Physically-adsorbed silane molecules initially attached to the outermost layers of the silane interphase were removed from the surface by washing with water whilst the chemically-adsorbed silane is retained at the surface. The amino groups of the coupling agent in the different layers are also different. In the chemisorbed layer, the amino groups form a hydrogen-bonded structure to the surface and in the physisorbed layers both free and hydrogen-bonded amino groups exist. Therefore, the above observation strongly supports the fact that the silane molecules are bonded firmly to the corona-treated polymer surface through chemical and hydrogen bonds.

Some preliminary work has also been done with XPS analysis of the γ-APS silanized LDPE. Figure 5 illustrates the XPS spectrum of the N(1s) peak of the γ-APS silanized LDPE. Two components for N(1s) 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.

Plasma treated LDPE The FTIR-ATR spectra of the LDPE treated by air, ammonia and heptylamine plasma are given in Figure 6.

Changes in the IR spectrum of LDPE film after treatment in air were only detected between 1750 and 1600 cm^{-1}. The band at 1720 cm^{-1} is due to carbonyl groups and the 1630 cm^{-1} band is probably attributed to C=C or amino groups. Both plasma treatment in ammonia and in heptylamine resulted in an absorption band at about 1640 cm^{-1}, which is probably due to the primary or secondary amino groups. Also, in the case of heptylamine plasma treatment, there is a broad peak centred at about 3350 cm^{-1} which might be the stretching band of the amine groups.

Adhesive Bonding

The efficiency of the new surface treatment in terms of adhesion enhancement was assessed by comparative studies of adhesively-bonded lap-shear specimens. The LDPE substrates, prior to bonding, were treated using the following surface treatment techniques:

(a) corona discharge only: 8.7 to 755 mJ/mm^2
(b) SICOR treatment, *i.e.* surface silanization comprising two consecutive steps:
  —corona discharge treatment: 8.7 to 755 mJ/mm^2
  —silane: 0.1% γ-APS
(c) plasma treatment

Bonding with methacrylate adhesive All solely corona discharge treated and "SICOR" silanized (corona + silane) LDPE substrates were bonded using a Permabond F241 methacrylate adhesive. Figure 7 illustrates the influence of the treatment energy level (energy per area unit) on the strength of the adhesive bond. It can be seen that an increase of the bond strength with increasing treatment energy is significantly greater for silanized LDPE surfaces, when compared with the solely corona discharge treated materials. The degree of adhesion enhancement can be illustrated by comparing the initial treatment energy required to obtain the bond exhibiting a strength of 3 MPa. Silanized LDPE requires an energy output equal to 27 mJ/mm^2 whilst the solely corona treated substrate requires 755 mJ/mm^2 to obtain the same bond strength.

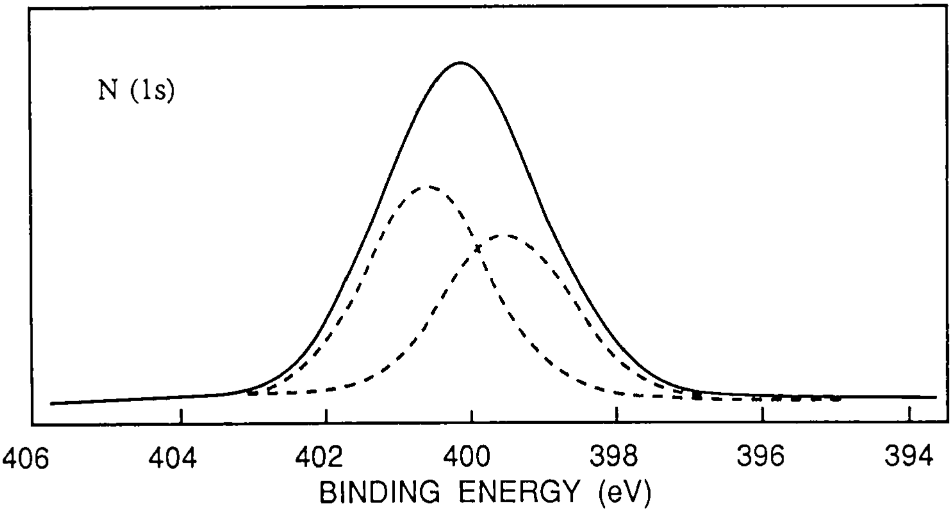

FIGURE 5 XPS spectrum of the N(1s) peak of the γ-APS silanized LDPE.

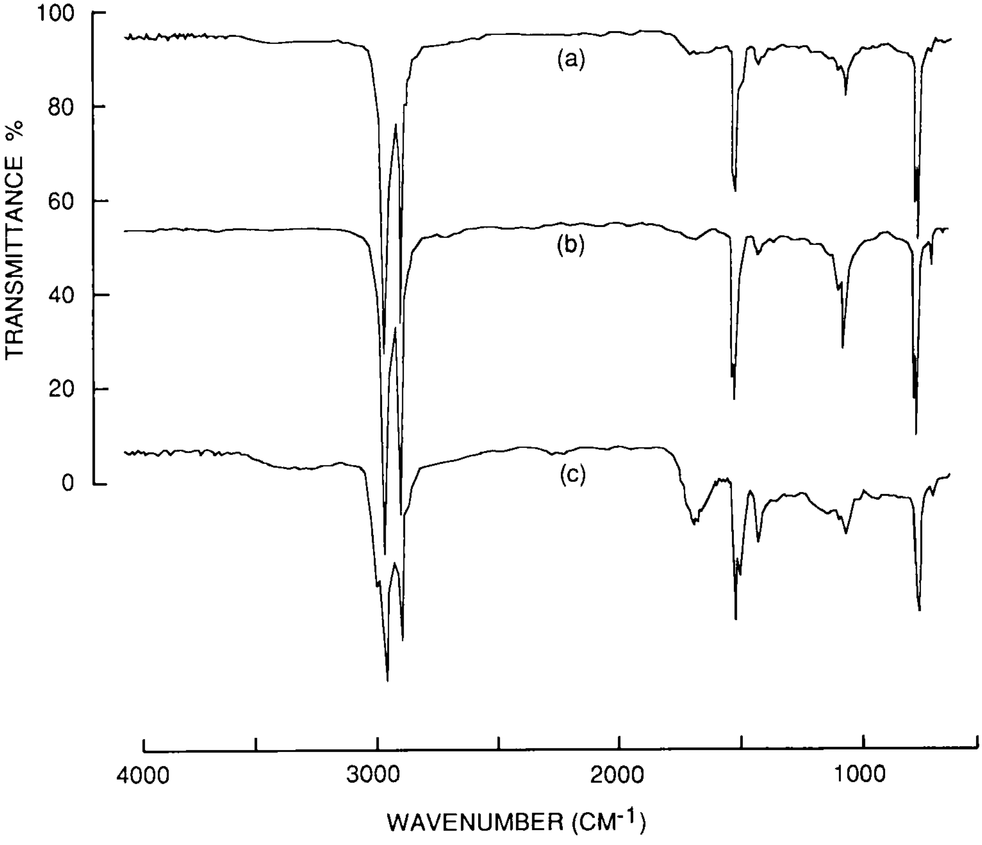

FIGURE 6 FTIR-ATR spectra of LDPE treated with various plasmas: (a) air plasma; (b) ammonia plasma; (c) heptylamine plasma.

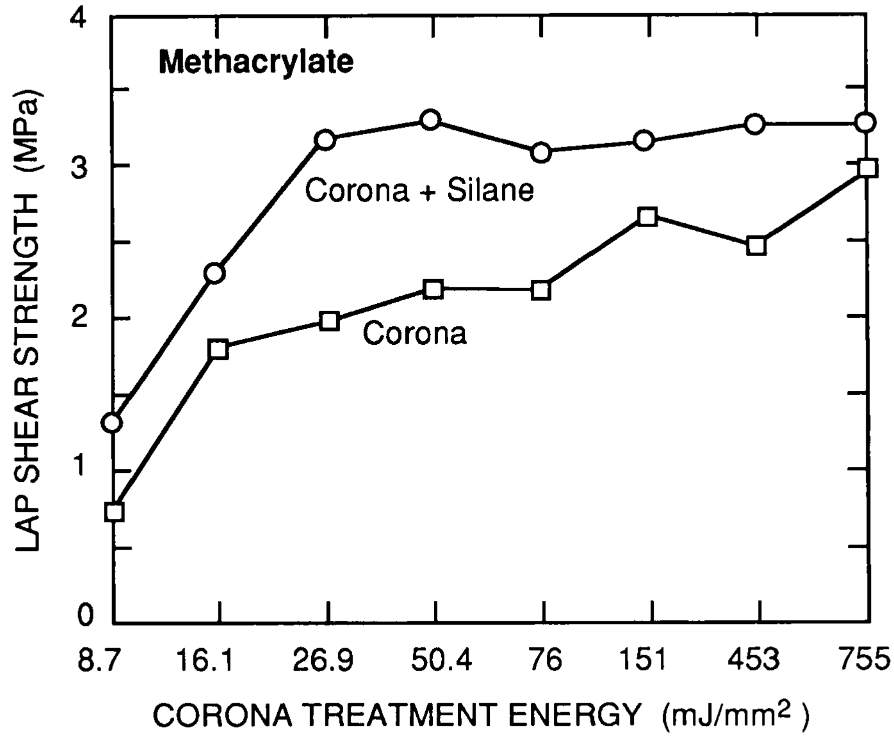

FIGURE 7 Variation of the lap shear strength of LDPE/Permabond F241 methacrylate adhesive bonded assemblies as a function of the energy level of corona discharge treatment.

The significant bond strength improvement for γ-APS silanized substrate bonded with methacrylate adhesive may be partially attributed to the fact that condensation products of amines and aldehydes act as curatives in acrylic technology.[28] It is possible, therefore, that the amino functional groups on the surface of the γ-APS silanized substrate participate in the curing process of the adhesive, additionally increasing the strength of the bond across the substrate and adhesive.

The ammonia plasma treatment was carried out using a power consumption of 35 W and a treatment time of 150 s. The strength of the adhesive bond with the substrates treated under these conditions is 1.6 MPa which constitutes only 50% of the bond strength obtained after the LDPE silanization using γ-APS. This relatively low bond strength after ammonia plasma treatment may be attributed to two factors: lower surface concentration of amino groups on LDPE after ammonia plasma treatment, compared with γ-APS silanization, and/or the possible overtreatment of the substrates due to prolonged exposure to plasma. These explanations, however, require further investigation.

Bonding with cyanoacrylate adhesive The efficiency of the new process described in this paper was assessed using substrates treated by various techniques described earlier, as well as those which were primed with an amino-based polyolefin primer, "Loctite 770," recommended for enhancing adhesive bonding of polyolefins with cyanoacrylates. The most detailed study was carried out using Loctite 406 adhesive. The results obtained with this material are representative for this generic type of adhesive.

Figure 8 illustrates the relationships between the bond strength and the energy level of corona discharge treatment. It can be observed that even a very low exposure level (8.7 mJ/mm^2) significantly increases the strength of the solely corona-treated material compared with the untreated one. However, it can also be seen that the additional surface silanization of the same low energy treated substrate (8.7 mJ/m^2+0.1% γ-APS) results in a remarkable 220% bond strength increase. It is interesting to note that for the solely corona discharge treated LDPE there is no further strength increase within the region 16 to 150 mJ/mm^2, with increasing treatment energy. Also, any energy level exceeding ~150 mJ/mm^2 leads to inferior bond strength with the strength decreasing with increase of the treatment level. Analysis of surfaces of LDPE treated at 450 mJ/mm^2, or higher, revealed the presence of uncured adhesive. This is presumably the result of a change in the chemical character of the LDPE surface which becomes acidic upon exposure to a high level of corona discharge energy. The above-mentioned suggestion is consistent with the

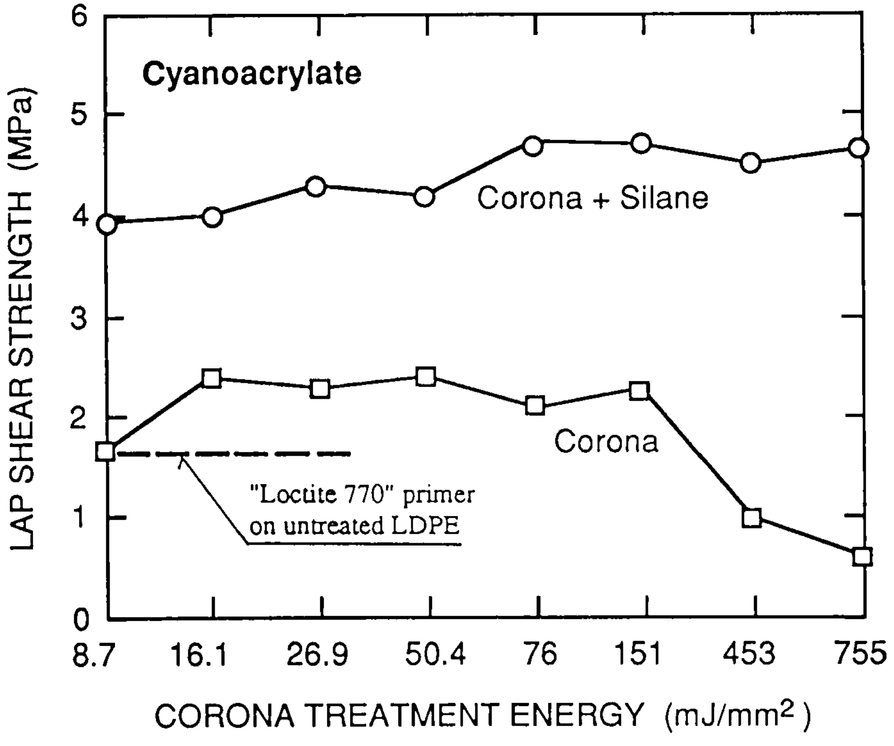

FIGURE 8 Variation of the lap shear strength of LDPE/Loctite 406 cyanoacrylate adhesive bonded assemblies as a function of the energy level of corona discharge treatment.

commonly-observed undercure or absence of cure of cyanoacrylate adhesives in contact with acidic surfaces.

A totally different situation is observed for γ-APS silanized LDPE surfaces bonded with the same type of adhesive. Regardless of the discharge energy level associated wih the first step of the "SICOR" process, there is always an about 200% or greater strength increase for silanized LDPE, with no strength decrease for high treatment energy levels as was observed for the solely corona treated LDPE. This indicates that after the surface silanization with the use of an amino-functional silane, *e.g.* γ-APS, the surface changes its character from acidic, as exhibited by solely corona treated LDPE, to basic after the amino-functional silane reaction with the oxidized polymer surface. The strength increase observed for the surface silanized with amino-functional silanes may also be partially attributed to the fact that amino-functional compounds enhance the cure process and crosslinking of cyanoacrylate adhesives.[29]

The LDPE samples were also treated by plasmas in various atmospheres, *viz.* ammonia, air and heptylamine, prior to bonding with cyanoacrylate, methacrylate and polyurethane adhesives. The results reported in Table I indicate that the bond strength of prolonged ammonia plasma treated (20 min) LDPE bonded with cyanoacrylate adhesive decreases by 50% compared with the 150 s treatment. This is probably due to the fact that the polymer surface was overtreated, causing damage in the superficial region of the sample. It may also be due to a loss of the mechanical properties of the material by the cutting of macromolecular chains into small pieces or by ablation. Similar observations have been made by Foerch *et al.*[30] Otherwise, the shorter ammonia plasma treatment (150 s) resulted in a significant improvement of adhesion with the cyanoacrylate adhesive, for which the strengths are comparable with those of LDPE treated by corona plus amino-silane treatments. Remember that, in both cases, the FTIR-ATR analysis showed the creation of surface amino functional groups, which, for the reason outlined previously, could be responsible for an additional improvement of the bond strength of LDPE to the cyanoacrylate adhesive. The bond strength of NH_3 plasma treated substrates subsequently bonded

TABLE I
Effect of plasma treatment of LDPE in various atmospheres on the strength of lap-shear specimens bonded with various adhesives

LDPE treatment	Adhesive	Bond strength [MPa]
NH_3 plasma 150 s	methacrylate (F241)	1.6
	cyanoacrylate (406)	4.5
NH_3 plasma 20 min	cyanoacrylate (406)	2.5
Air plasma	polyurethane (Tyrite 7460)	2.6
	methacrylate (F241)	1.3
	cyanoacrylate (406)	2.7
Heptylamine plasma 10 min	cyanoacrylate (406)	0.4
Heptylamine plasma 20 min	methacrylate (F241)	0.5
	cyanoacrylate (406)	0.5

with the methacrylate adhesive is significantly lower than that of the "SICOR" treated material (see Figure 7), in which the corona treatment step was carried out at an energy level equal to or greater than 26.9 mJ/mm^2.

For air and heptylamine plasma, the improvements in the adhesion of LDPE to different adhesives were insignificant. Although amino functional groups were found on the surface of LDPE treated by heptylamine plasma as shown by FTIR-ATR, it is likely that most of them were inaccessible due to the steric effect produced by the long chain alkyl, which resulted in the loss of efficiency for this type of treatment. It is also possible that the relatively long treatment time in our experiments resulted in a partial decomposition of the functional groups initially introduced onto the surface.

The strength data on air plasma treated LDPE in Table I show a relatively low efficiency for this treatment under the set of conditions chosen in our work. Comparison of these results with Figures 7 and 8 relating to corona and "SICOR" treatment indicates that the strength of air plasma treated assemblies subsequently bonded with the cyanoacrylate and the methacrylate adhesives is similar to that exhibited by low-energy corona discharge treated substrates. In the absence of XPS and other surface analytical data, we cannot, at this stage, offer a detailed explanation for this, since the mechanisms and possibly final surface modification effects in air plasma and air-corona treatments are dissimilar in terms of the composition of the atmosphere, *i.e.* the type and quantity of active species present in the ionised glow or discharge zone in both processes. These, in turn, may subsequently affect both the type and the density of the surface functional groups incorporated onto the substrate surface despite the fact that both of them are carried out in the air atmosphere.

It is also shown in Figure 8 that the LDPE primed with the Loctite 770 polyolefin primer results in relatively low strength increase, in comparison with the "SICOR" silanization of the substrate.

Bonding with polyurethane adhesive A two-part polyurethane adhesive, Tyrite 7460 A/B (Lord), was used in this study. The results regarding the influence of various types of surface treatment on the bond strength are illustrated in Figure 9. Untreated LDPE produces a very low bond strength of 0.3 MPa. Due to the chemistry of polyurethane adhesives, the incorporation of hydroxyl groups onto the polymer surface after oxidative surface treatment, *e.g.* corona discharge or air plasma, is sufficient to result in the creation of strong urethane linkages between an oxidized LDPE surface and the adhesive, thus resulting in a high strength adhesive bond on solely oxidized (*e.g.* corona treated) polymer.

Further studies carried out with the "SICOR" silanized surfaces point out the importance of choosing a silane with the optimum functionality for enhancing adhesion of polyurethane adhesives. When the amino-functional silane γ-APS was used for LDPE silanization, the decrease in the number of surface OH— groups available for formation of urethane linkages, and associated with its substitution of surface hydroxyl groups by amino groups, proved not to be beneficial to the bond strength which was approximately the same for both solely corona treated and "SICOR" silanized LDPE. However, the use of a chloropropyltrimethoxy silane, Z-6076

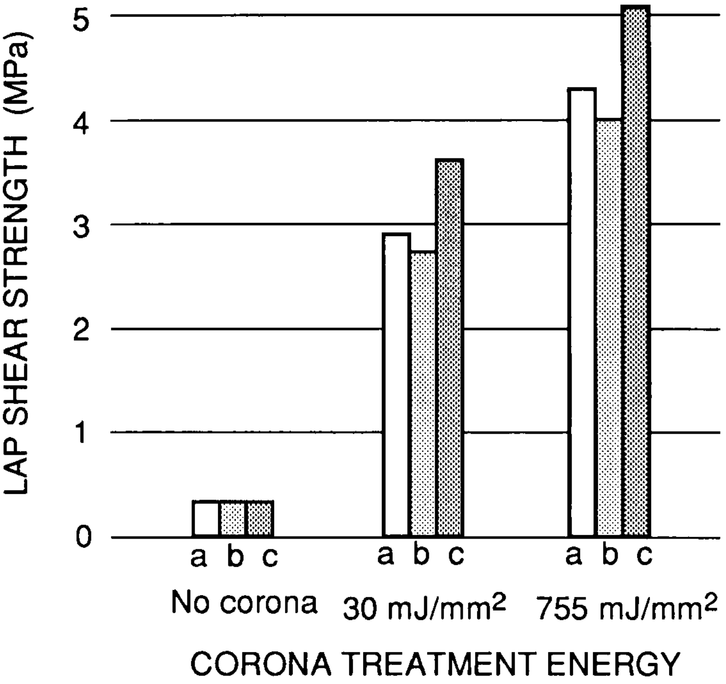

FIGURE 9 Variation of the lap shear strength of LDPE/Tyrite 7460 polyurethane adhesive bonded assemblies as a function of pre-treatment type and the energy level of corona discharge treatment: (a) no silane; (b) corona discharge + 0.1% γ-APS (Dow Corning Z-6020 silane); (c) corona discharge + 0.01% chloropropyltrimethoxy silane (Dow Corning Z-6076 silane).

(Dow Corning), for surface silanization leads to a noticeable improvement of the bond strength (approximately 20–30%) compared with the solely corona treated substrates (see Figure 9).

CONCLUSIONS

1. A novel surface engineering technique for polymers comprising surface oxidation (*e.g.* by corona discharge treatment, air plasma, etc.) and organo-silane deposition provides a very effective means for enhanced adhesion of low density polyethylene with a range of typical engineering adhesives.
2. The comparative study on the process effectiveness involving: polyolefin primer Loctite 770, corona discharge, surface silanization (corona discharge + silane) and various plasma treatments, indicates that the process developed and described in this paper, *i.e.* surface silanization through the corona plus silane treatment, gives significantly improved bond strength over polyolefin primer or corona treatment alone, and results at least as good as, or better than, plasma treatments investigated in this work.

References

1. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mater. Sci.* **11,** 1270 (1976).
2. P. Blais, D. J. Carlsson, G. W. Csullog and D. M. Wiles, *J. Colloid Interface Sci.* **47,** 636 (1974).
3. D. Briggs, V. J. I. Zichy, D. M. Brewis, J. Comyn, R. H. Daham, M. A. Green and M. B. Konieczko, *Surface Interface Anal.* **2,** 107 (1980).
4. A. Bradley and T. R. Heagney, *Anal. Chem.* **42,** 894 (1970).
5. H. Schonhorn and F. W. Ryan, *J. Appl. Polym. Sci.* **18,** 235 (1974).
6. L. Lavielle and J. Schultz, *Bull. Soc. Chim. France* **6,** 1119 (1985).
7. C. E. M. Morris, *J. Appl. Polym. Sci.* **14,** 2171 (1970).
8. C. E. M. Morris, *J. Appl. Polym. Sci.* **15,** 501 (1971).
9. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mater. Sci.* **14,** 1344 (1979).
10. F. Garbassi, E. Occhiello and F. Polato, *J. Mater. Sci.* **22,** 207 (1987).
11. D. K. Owens, *J. Appl. Polym. Sci.* **19,** 265 (1975).
12. C. Y. Kim, J. Evans and D. A. I. Goring, *J. Appl. Polym. Sci.* **15,** 1365 (1971).
13. J. R. Hall, C. A. L. Werterdahl, A. T. Devine and M. J. Bodnar, *J. Appl. Polym. Sci.* **13,** 2085 (1969).
14. K. Rossmann, *J. Polym. Sci.* **19,** 141 (1956).
15. E. M. Liston, *J. Adhesion* **30,** 199 (1989).
16. H. Griesser, in *Polymers in Information Storage Technology,* K. L. Mittal, Ed. (Plenum Publ. Corp, New York & London, 1989), p. 351.
17. R. Foerch, N. S. McIntyre and D. H. Hunter, *Kunststoffe-German Plastics* **81,** 260 (1991), 3.
18. W. Gutowski, *CSIRO DBCE,* MM/RR, Vol. 3, 232, (June 1989).
19. W. Gutowski, *CSIRO DBCE,* MM/RR, Vol. 4, 3, (July 1989).
20. W. Gutowski, *CSIRO DBCE Doc.* TW162/2/11. "A Method of Surface Treatment of Polymeric Materials and Fibres, including Carbon and Graphite Fibres." Provisional Patent Application, Australia—Note (December 1989).
21. W. Gutowski and E. R. Pankevicius, *Composite Interfaces* **1, No. 2,** 141 (1993).
22. C. R. Choe and J. Jang, in *Controlled Interphases in Composite Materials,* H. Ishida, Ed. (Elsevier, New York, Amsterdam & London, 1990), p. 97.
23. N. Inagaki, S. Tasaka and H. Kawai, *J. Adhesion Sci. Techol.* **6**(2), 279 (1992).
24. D. J. Hook, T. G. Vargo, J. A. Gardella, Jr., K. S. Litwiler and F. V. Bright, *Langmuir* **7,** 142 (1991).
25. H. Griesser, *Vacuum* **39,** 489 (1989).
26. S. Naviroj, J. L. Koenig and H. Ishida, *J. Macromol. Sci.-Phys.* **B22**(2), 291 (1983).
27. S. R. Culler, H. Ishida and J. L. Koenig, *J. Colloid and Interface Sci.* **106**(2), 334 (1985).
28. C. W. Boeder, in *Structural Adhesive-Chemistry and Technology,* S. R. Hartshorn, Ed. (Plenum Press, New York & London, 1986), p. 217.
29. P. F. MacDonnell, in *Adhesion-15,* K. W. Allen, Ed. (Elsevier Applied Science, London, 1991), p. 69.
30. R. Foerch, J. Izawa and G. Spears, *J. Adhesion Sci. Tech.* **5**(7), 549 (1991).
31. D. Y. Wu, W. Gutowski, H. Willis and G. George (Prepared for publication in *J. Adhesion Sci. Technol.*).