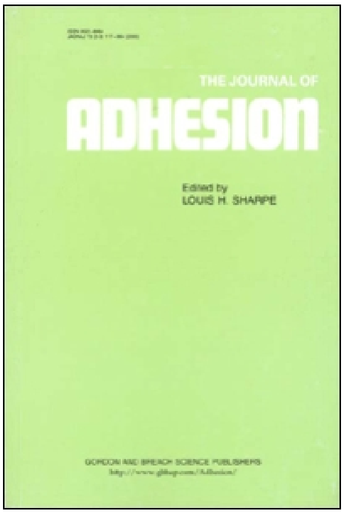

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Air-plasma Pre-treatment for Polypropylene Automotive Bumpers

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The effect of forced air-plasma pre-treatment, Lectro-treat^{TM}*, on polypropylene has been investigated using X-ray photoelectron spectroscopy (XPS), angle-resolved XPS (AR-XPS), and atomic force microscopy (AFM). The pre-treatment process is found to induce both surface chemistry changes and topographical changes. The parameters of the pre-treatment process can be optimised from these observations. The Lectro-treat pre-treatment process has been used for adhesive bonding of a demonstrator component: a bumper assembly. The adhesively bonded bumpers performed successfully in standard automotive tests.*

Keywords: Atomic force microscopy; Polypropylene; Surface treatment; X-ray photoelectron spectroscopy

1. INTRODUCTION

Polypropylene is becoming increasingly used throughout industry due to its low cost and useful properties compared with similar materials. However, the difficulty of bonding polypropylene (PP) is holding back usage of this versatile material. Polypropylene has many desirable properties which both the automotive industry and others are interested in exploiting. These include low density, inertness, corrosion resistance, and ease of recyclability. Recylability allows mass-produced parts to be created with little wastage and at a minimal unit

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cost, whilst also allowing manufactured components at the end of their lifetime to be re-used in some capacity. The melt flow characteristics of polypropylene mean that complex shapes can be easily moulded in a variety of intricate shapes, large and small, by virtually every moulding process.

Before polypropylene can be used as a structural component within a vehicle it must be possible for the component to be joined by a variety of methods to other parts of the vehicle. Traditional methods such as mechanical fastenings, using rivets and bolts, lead to stress concentrations causing delimitation and distortion of the area adjacent to the joint. Adhesive bonding has, therefore, been put forward as a possible method of joining polypropylene to itself and dissimilar materials [1].

The improvement of the surface energy of polypropylene has been the subject of many different research projects and, as such, two main avenues have been explored. The first is that of creating an alternate face of high bondability and wettability to the applied adhesive, whilst also maintaining a good bond to the underlying polypropylene substrate. This route has been carried out by the use of coatings such as organosilane primers invented by the aircraft industry for bonding of glass and glass fibers. Other forms of alternate interface also include copolymers, grafting, metallization, transcrystallisation [2] and the modification of the chemical composition of the polypropylene to increase the number of bond sites. The second avenue of research is centered upon surface modification of the original polypropylene by the use of various energetic surface pre-treatments. There are many differing types of pre-treatments, which range from those which modify the surface topography, so increasing bondable area, to those which modify the top surface layer chemically. Cold plasma treatment has been shown to enhance the wettability of polypropylene surfaces [3] and such surface modification has been shown to increase peel strength [4]. Plasma treatment of polypropylene has been shown to lead to effective bonding of surface coatings [5].

This paper includes some selected results from a large collaborative project which was supported by EPSRC* as part of the EPSRC/DTI Lightweight Vehicle Initiative. The overall aim of the project was to identify suitable adhesion bonding processes for future generations of UK manufactured vehicles. The project included both different adhesives and different pre-treatments. The most promising approach finally identified was the use of forced air-plasma pre-treatment with a polyurethane adhesive. This adhesive system was applied to a demonstrator component: a polypropylene bumper shell and its

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*Engineering and Physical Sciences Research Council (UK).

reinforcer. The assembly was tested according to standard automotive impact tests.

2. EXPERIMENTAL DETAILS

2.1. Materials

The polypropylene used was a prototype talc-filled grade, Sequel SQ1450E, provided by Solvay Engineered Polymers (Alpharetta, GA, USA). The authors understand that this material was designed for high impact performance for applications such as automotive bumpers. No further chemical information regarding this material was available. The adhesive used was a 1-part polyurethane adhesive, Betaseal 1780 from Gurit Essex (now Dow Automotive, Auburn Hills, MI, USA). This adhesive was extensively tested within this project. Although its uniaxial strength was found to be low, its value of critical fracture energy, measured using peel tests, was found to exceed the value for many epoxy structural adhesives [6]. This adhesive was considered to be very suitable for the bonding of an automotive bumper subjected to impact tests.

2.2. Forced Air-Plasma Pre-Treatment

Lectro-treat$^{\mathrm{TM}}$ blown air plasma system (Lectro Engineering, St. Louis, MO, USA) was used to pre-treat the surface of polypropylene. There are two different techniques for application of this pretreatment, the tunnel treatment and the gun treatment. The tunnel treatment allows easy 3-D sample treatment for a range of materials. This system uses large capacitor plates, with an applied voltage of 120 kV to induce a corona to form between the plates, which are 1 foot (30.5 cm) apart. Samples are fed through the system using a stepping motor driven conveyor belt, whose speed can be varied. The gun treatment is a hand-held or robot controlled system; an example of its use is shown in Figure 1. Two wire electrodes within the unit are connected to the secondary winding of a high voltage (12–15 kV) transformer. Electric arc sparks are formed between the electrodes at a rate of around 50–60 arcs per second, and air is blown through the arcs. The appearance can be described as a “cold flame”. The virtually constant air plasma is loaded with energetic ions. This is a low temperature process with no fire hazard or melting problems.

The parameters which could be varied for this surface pre-treatment were the speed of the treatment and the angle of the gun. These parameters were optimized using mechanical testing of single lap-shear

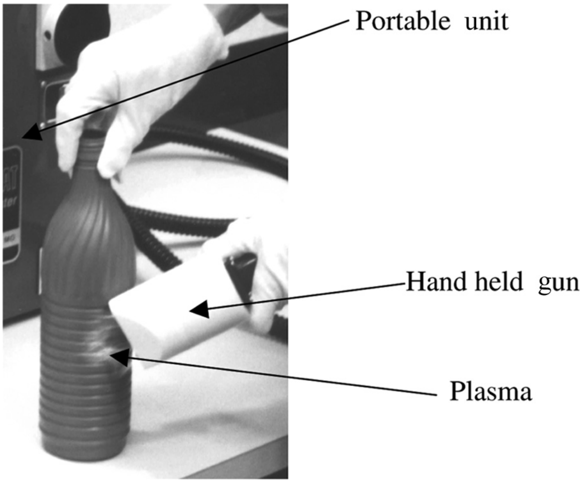


FIGURE 1 Lectro-Treat^{TM} pre-treatment gun.

joints. It was concluded that the angle of the gun did not affect the quality of the pre-treatment. The optimum speed obtained from the mechanical tests was between 1 and 2 ft/min (0.31 and 0.61 m/min) [7].

2.3. Surface Analysis

X-ray photoelecton spectroscopy (XPS) was used to examine the chemistry of the treated surfaces. The X-ray photoelectron spectroscopy (XPS) spectra were acquired using a VG Scientific ESCALAB MKII (Thermo Fisher Scientific, Waltham, MA, USA), operated in constant analyser energy mode, at a pass energy of 50 eV for wide scan survey spectra and 30 eV for higher energy resolution region scans. A Mg Kα source operating at 300 W (20 mA; 15 kV) was used and the take-off angle maintained at 90° for chemical analysis. Digital acquisition was achieved with a VGS 5250 data system based on a DEC PDP 11/73 computer interfaced to the spectrometer.

Angle-resolved XPS (AR-XPS) was used to carry out depth profiling. The application of this technique for polymeric materials is described by Woodruff and Delchan [8]. This technique is capable of ultra-high resolution chemical analysis within the very near surface region, analysing a range between 2–10 nm in depth. The sample is mounted on a smaller than normal stub to prevent contact with equipment within the small space of the chamber. Once the samples are in the chamber the analysis is run as normal for each angle. The sample holder is rotated at set angle intervals [9].

The depth of analysis can be calculated from knowledge of the material and angle; the method has been described in detail by Watts [10]. The calculation of depth is carried out by comparison of signal intensities at certain depths *via* a modification of the well known Beer-Lambert equation:

$$I_{\mathrm{d}} = I_{\infty} \exp(-\mathrm{d}/\lambda \sin\theta),$$

where I_{d} is the intensity at analysis depth d, I_{∞} is the intensity from an infinitely thick clean substrate, d is the analysis depth, λ is the electron attenuation length for a particular electron, and θ is the electron take-off angle from the substrate.

Atomic force microscopy (AFM) was used to probe the topography of the surface and to measure the roughness. The polypropylene substrates used for these analyses were Homopolymer HF 135 M (Borealis AG, Vienna, Austria). The plaques were specially moulded against cleaved mica at very high packing pressures, to ensure an atomically smooth surface with minimal shrinkage. Samples were manufactured 80×40 mm in size, with an imagable area of approximately 30×20 mm available for AFM. The instrument used was a Digital Instruments Dimensionscope II (Santa Barbara, CA, USA).

3. RESULTS OF THE SURFACE ANALYSIS

3.1. Wettability

Initial tests for the effect of pre-treatment were carried out through approximate measurement of the surface energy using wettability inks (Dyne Technology, Litchfield, UK). It was found that the surface energy with all pre-treatment speeds was nearly water wet, exceeding $70\,\mathrm{mJ/m^2}$. These high values would be considered in the pre-treatment industry to indicate fully treated surfaces.

3.2. Surface Analysis Using XPS

The results of the surface chemical analyses using 90° take off angle are summarised in Figure 2, with the average atomic compositions plotted for each pass speed. All results presented are average results gained from analysis of between four and seven specimens; the scatter between nominally identical specimens was below 1 atomic %. The pre-treatment using Lectro-treat was found to be very effective, with even fast pass speeds inducing levels of surface modification above that of more traditional pretreatment types such as corona discharge [11]. The level of oxygen content was found to decrease with increasing

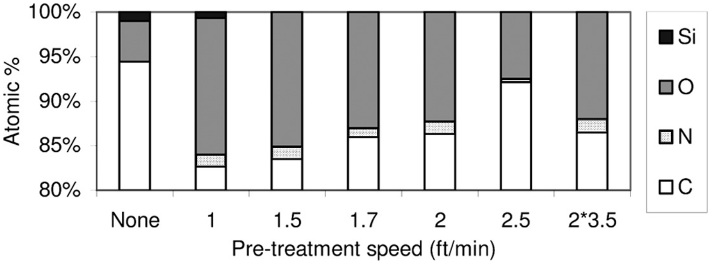
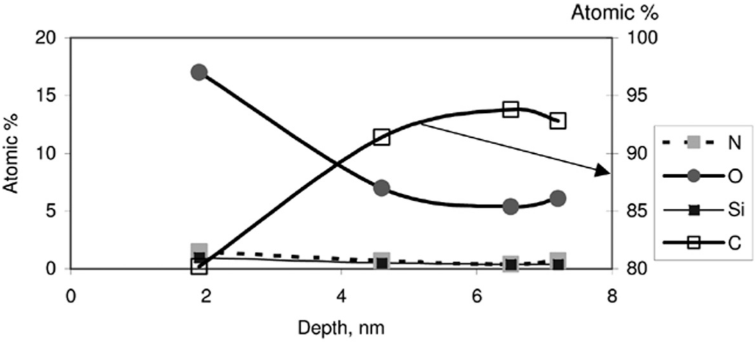
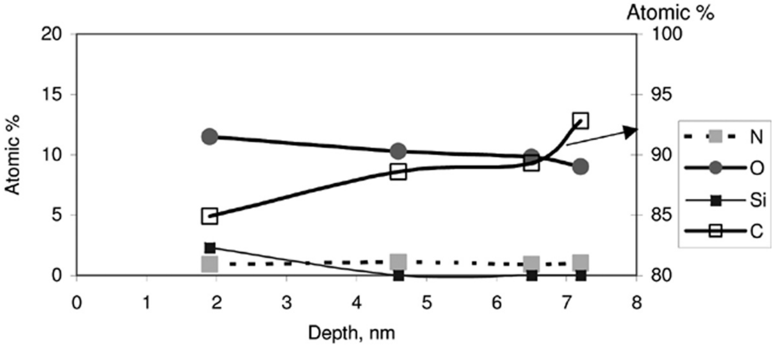


FIGURE 2 Results from XPS analysis for different pre-treatment speeds.

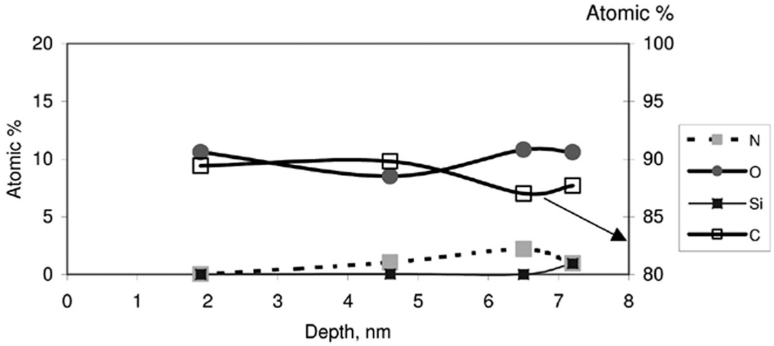


(a)

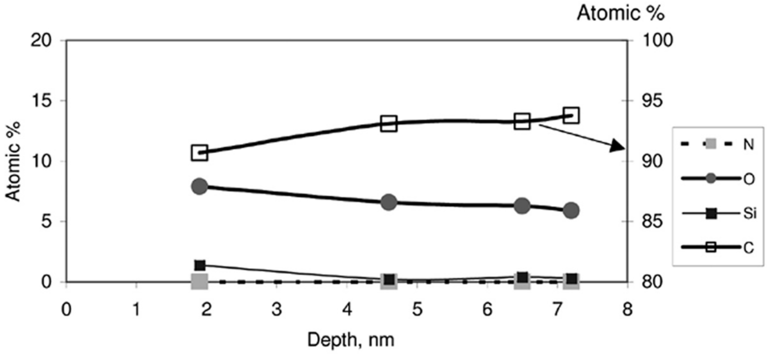


(b)

FIGURE 3 Depth profile XPS results: (a) 1.0 ft/min (0.31 m/min); (b) 1.5 ft/min (0.46 m/min); (c) 2.0 ft/min (0.61 m/min); (d) 2.5 ft/min (0.76 m/min).



(c)



(d)

FIGURE 3 Continued.

pass speed, indicating that the pretreatment required is not complete. Multiple passes at 3.5 ft/min (1.07 m/min) were found to increase the level of oxygen content to 12%, higher than that predicted by the trend for such a pass speed but lower than the oxygen content of 13% gained from the single pass at 1.7 ft/min (0.52 m/min) taking the same period of time. The nitrogen content was found to remain at a similar level, between 0.4 and 1.5%, regardless of pretreatment speed. The maximum level of oxygen inducement was found to be at speeds of 1 and 1.5 ft/min (0.46 m/min) 15.2%. These observations are in agreement with the experimental measurements of bond strength [7].

The results from the depth profiling are shown in Figures 3a–d. The surface modification caused by the Lectro-treat process was found to be very surface sensitive, with both oxygen and nitrogen induced in regions very near the surface, compared with more robust plasma techniques such as vacuum plasma [11]. The pre-treatments were found to be of higher oxygen content for slow pass energies, for example 17% at 1.9 nm for the slowest speed. However the slow pass energies were found to pre-treat more material closer to the surface. The level of modification decreases rapidly with depth, for speeds 1.5 ft/min (0.46 m/min) and below. All the substrates pre-treated were found to have a minimum level of at least 6 atomic % carbon at the deepest penetration depth. However, surface penetration by the oxygen and nitrogen species is relatively low, decreasing rapidly at depths beyond 4.6 nm, indicating that the power of the plasma is not as high as the vacuum process and flame processes [11]. The near surface oxygen content is very high for the most effective pre-treatment speeds: above 16 atomic % which is far above that normally found with any pre-treatment of polypropylene.

All the depth profiles show that the main average oxygen concentration is found at around 4 nm or above, regardless of pre-treatment speed. The depth profile plots also show that the nitrogen concentration decreases less dramatically than that of the oxygen species. The oxygen being closer to the surface and at highest concentration makes this the almost exclusive chemical bonding mechanism for any adhesive.

3.3. Surface Analysis Using AFM

The pre-treatment speeds imaged were untreated, 2.0 ft/min (0.61 m/min) (slight under treatment), 1.5 ft/min (0.46 m/min) (optimum treatment), and 0.5 ft/min (0.15 m/min) (severe over treatment). Analysis of untreated substrates, moulded against cleaved mica, showed that the surface was very flat, with a z-axis height range of only a few nanometers.

Examples of AFM images from the three conditions are shown in Figures 4a–c. An approximate z-axis scale is shown on these figures; the accuracy of this scale is limited from the analytical software available. It was found that the Lectro-Treat technique induced significant amounts of topographic surface modification to the polypropylene surface. Surface roughening is observed on two differing scales. Both forms of roughening were found to be induced almost instantly by the treatment and then exaggerated with increased pre-treatment time.

The first form of induced topography was found to be large nodules, similar in scale to that of the nodules identified previously for flame and vacuum plasma treatment [11]. The second form of topography induced is in the form of nano-pits, which are formed across the surface of the substrate. In some cases these nano-pits were found to ring the large nodules of un-etched material. In these cases the nodules appeared to be larger in height. In this manner the nodules increased in size with increased pre-treatment time. The nano-pits were found to

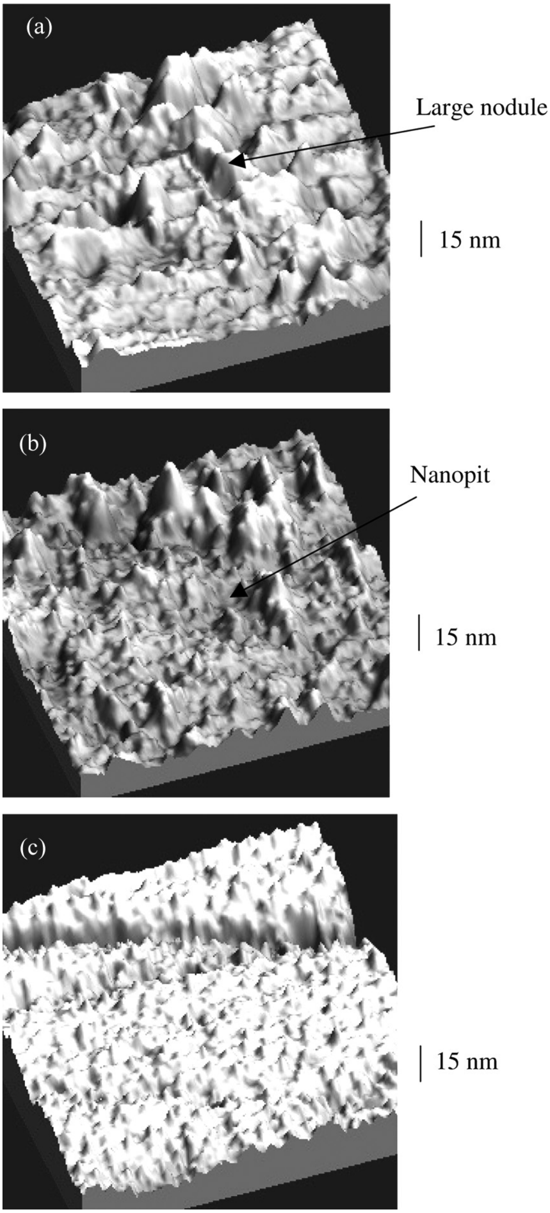


FIGURE 4 AFM 10 μm width scans for different levels of pre-treatment: (a) 2.5 ft/min (0.76 m/min) (Slight under-treatment); (b) 1.5 ft/min (0.46 m/min) (Optimum speed); (c) 0.5 ft/min (0.15 m/min) (Severe over-treatment).

be present at all pre-treatment speeds. At fast pre-treatment times the pits were found to be small, in both diameter and height. At longer pre-treatment times these nano-pits were shown to increase slightly in diameter, whilst increasing substantially in depth. When a region has a high concentration of nano-pits, it was found that the whole surface regions' height compared with the z-axis decreased and became negative. These regions were termed depressions and it is surmised that they are created because of material weaknesses in this region. This may be due to crystalline form, moulding characteristics such as transcrystallinity, or a region of particularly low polymeric weight material. These nano-pores were also found to surround some of the large nodules. In this manner, as the pits coalesce the peak-to-trough height is increased and, hence, the size of the nodule is intensified.

Within the superstructure of other etched systems a polarity exists, with the top peaks having a particular charge whilst the bottom pores have a differing opposite charge. However, the total charge across the surface is zero, unless a potential is placed on the surface. With the Lectro-treat it has been shown that pits exist on the surface and increase in depth with increased pre-treatment. However, it is evident from the process employed that no superstructure is created except in chemical terms as investigated using AR-XPS. Taking into account the high electrical charge inherent in this process, we postulate that polarity in the surface may be induced. Such polarity could account for the very high values of wettability obtained for this treatment (see Section 3.1). Polarity in the surface can provide an additional bonding mechanism. However, experimentation of this hypothesis was outside the ability of the equipment available to this project.

4. TESTING THE BUMPER ASSEMBLY

The bumper assembly is shown in Figure 5. It consists of a polypropylene shell and a polypropylene reinforcer. These parts are traditionally held together using friction welding. However, this process leaves swarf (fine filings and shavings) on the surface which may affect the surface finish of the paint. Adhesive joining would be a preferred method. All of the assemblies tested had the geometry shown in Figure 5.

The Lectro-treat surface pre-treatment was carried out on the bumper surface using a pretreatment gun attached to a robot arm using the optimized parameters which had been deduced from the surface analysis. The adhesive was heated in an oven at 50°C for 1 hour, before

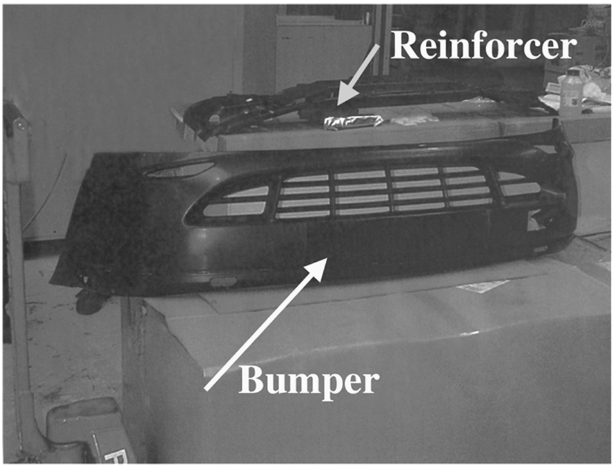


FIGURE 5 The Bumper assembly.

application to the surface using a pneumatic applicator gun. This resulted in a triangular bead of adhesive approximately 6 mm high. The reinforcer was positioned by hand. The assembly was left to cure for 2 weeks in ambient conditions.

The assembled bumpers were subjected to four different conditions before testing; a minimum of three assemblies were tested at each condition. All tests were carried out at approximately ambient temperature. The conditions used were: ambient conditions; subjected to 90-hour standard automotive durability cycle [7]; stored at −20°C for a minimum of 1 hour; stored at 70°C for a minimum of 1 hour. These tests conditions were chosen to represent the extreme of the conditions required for these assemblies. Front centre impact tests were carried out at Linpac Automotive (Dunstable, Bedfordshire, UK) at the standard impact speed of 2.5 km/hr. In order to pass this test, no part of the reinforcer must detach from the bumper shell. The results of these tests, compared with tests on the friction welded bumper assemblies, are summarized in Figure 6.

The results in Figure 6 show that the adhesively bonded bumper assemblies all passed the tests except after the high temperature treatment conditioning. Further inspection of this failure indicated that it had occurred within the treated layer on the bumper; the pre-treatment conditions may not have been optimized or the material may have been conditioned too close to its glass transition temperature. The test was passed by the adhesively bonded bumpers after low temperature conditioning; the friction welded bumpers failed after

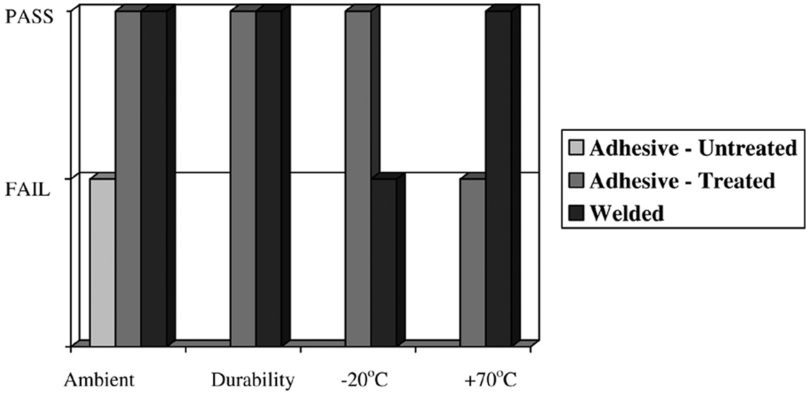


FIGURE 6 Results from the bumper trials.

this conditioning. The requirement for the pre-treatment is clearly shown from the results at ambient temperature.

5. CONCLUDING REMARKS

The effect of forced air plasma pretreatment, Lectro-treat, on polypropylene has been investigated using XPS and AFM. The results show that this pre-treatment has a potentially significant effect which may lead to the formation of good bonds, particularly for adhesives which bond through oxygen species. Further bonding may occur through polarity changes, but this hypothesis could not be further explored in this work. The surface modifications are only found in the very near surface regions. The effectiveness of this pre-treatment has been demonstrated *via* testing of a bumper assembly.

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