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Improving adhesion performance of polyethylene surfaces by cold plasma treatment

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Abstract In this paper, the effects of low pressure plasma treatment on surface energy of polyethylene samples and on shear properties of adhesive bonded joints based on these substrates have been investigated. In particular, the optimization of two plasma process parameters, exposure time and power input, was studied performing contact angle evaluation and lap-shear tests. The plasma treatment was also compared with a conventional primer treatment, for which it is a clean and effective alternative. As a measure of the durability of both treatments, the bond shear strength immediately after bonding was compared with that after a storage period in the laboratory environment. The experimental results show that the optimized plasma process may remarkably increase wettability properties of polyethylene surfaces and shear strength of bonded joints, even higher than those treated with primer and that these good properties remain quite unchanged even after some days of storage in a laboratory.

Keywords Cold plasma treatment · Adhesive bonding · Polyethylene · Contact angle

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1 Introduction

The application of polymeric materials is rapidly increasing in many industrial fields, such as medicine, automotive, aerospace and electronics, since they have excellent physical and chemical properties, are usually not very expensive and easy to process and recycle. Their extensive use in technical applications requires the possibility of being effectively joined to other components, in particular through adhesive bonding technique. Several studies on bonding techniques compared to welding and riveting have been conducted for a great number of materials and applications [1–3]. Indeed, adhesive bonding often provides structures that are mechanically equivalent to or stronger than conventional assemblies, at lower cost and weight. Not only do adhesives transmit stresses from one member of the joint to another much more uniformly than mechanical fasteners, but they also ensure acoustic insulation, vibration attenuation, reduction of corrosion problems and improvement of fatigue life [4–6].

For an effective application of polymers it is essential to have good adhesion behaviour to ensure good mechanical properties and durable components. Unfortunately, in general terms, polymers are characterized by high chemical inertia, which leads to very low surface energy values and, consequently, poor adhesive properties and this is particularly true for polyolefins [4, 5].

As a consequence, the surface preparation of polymeric adherends is extremely important in the adhesive bonding process [5].

Many approaches to surface treatments based both on chemical or physical modifications have been developed in recent years in order to improve the surface activity of polymers [7, 8]. Physical methods based on mechanical abrasion are supposed to extend bonding area as they increase the roughness, but cause extensive degradation to the specimens treated. On the other hand, chemical treatments are typically used with the aim of modifying both morphology and chemical structure of polymers, but they present serious environmental problems of waste disposal, which has moved investigations to an industrial alternative to these processes [4, 5, 8].

Therefore, the use of plasma sources has been consolidated as surface treatments since they are useful to modify the surface layers without affecting the bulk material properties and offer fast and environmentally friendly technology [9–25]. If we consider the different plasma treatments (corona, low-pressure glow discharge, atmospheric, etc.), the low-pressure glow discharge plasma, also called cold plasma, allows complete control of the processing parameters, and this leads to good homogeneity and reproducibility [26–28]. Furthermore, it promotes a remarkable increase in adhesive properties of polymer films in terms of wettability of the surface [12, 29]. It also offers a more long-lasting surface energy increase than any other treatment [30].

In the context of this study, cold plasma treatment was employed to modify polyethylene surfaces. The wettability of the specimens was estimated both for untreated and plasma treated specimens. The improvement in adhesion properties of these materials after plasma treatment was correlated with lap shear strength of adhesive bonded joints. The results were also compared with a conventional primer treatment.

2 Materials and methods

2.1 Materials

The material used for surface investigation and as substrate for adhesive bonded joint realization was high density polyethylene (HDPE). Every treatment came after a preliminary cleaning process with acetone, in order to eliminate grease or pollutant particles from the surfaces.

The adhesive selected was Loctite® 401™, a cyanoacrylate adhesive designed for the assembly of low surface energy materials. Supplier specifications suggest a cure time of at least 24 h, before full chemical and mechanical resistance development [31].

2.2 Surface pre-treatment

In this paper two types of preliminary surface treatment were compared: primer pre-treatment and plasma pre-treatment. Some untreated specimens were used as a basis for comparison.

The primer adopted was Loctite® 770 ™, which is specific to make polyolefin and other low energy surfaces suitable for bonding with Loctite cyanoacrylate adhesives [32].

For the evaluation of the effect of cold plasma treatment on polyethylene substrates, a large number of samples were exposed to radio frequency (RF) low pressure plasma, using air as working gas. A glow discharge RF generator operating at 13.56 MHz (Gambetti Kenologia, Italy) was used. The effect of two working parameters was investigated: power input and exposure time. The evaluation method information is reported in the paragraphs below. More details about the working parameters and the tests performed are presented in Table 1. Two parameters were kept fixed by the equipment: the flow rate of 25 cm^3 min^{-1} for the air input and the working pressure at 0.5 mbar.

Table 1 Working parameters for plasma pre-treatment and tests performed

Plasma working parameters			Test performed	
Power input (W)	Exposure time (s)	Ageing	Contact angle	Lap-shear test
50	5, 30, 60, 180, 300, 600	X (only 180 s)	X	X
100	5	X	X	X
150	5		X	
200	5		X	

2.3 Evaluation of contact angle

A significant parameter regarding the suitability of a surface to be bonded effectively is wettability [3]: if the adhesive wets the surface in an optimal way, the contact area increases and consequently the joint will withstand greater stress. Since polyethylene wettability is very poor [19, 24, 25], tests were carried out to verify the effects of both primer and cold plasma treatment on this parameter.

In particular the wettability of the substrate was evaluated by contact angle measurement. Demineralised water was dropped onto the surface of the sample using a calibrated pipette. All the measures were performed using a Leica Digital Microscope and X-Pro Software. At least three drops were measured and averaged on the samples treated.

2.4 Lap-shear test

Rectangular adherends, having dimensions 101.5 × 25.4 × 2 mm^3 were prepared with different types of treatment and parameters and bonded for single tensile lap shear tests. An overlapping of 12.5 mm was realized. Except for the sample thicknesses, the dimensions of the specimens refer to ASTM D 3163 [33] standard, as well as the lap-shear tests conditions; five samples for each parameter setup were tested and averaged. Every shear strength value was calculated referring to the real bonding area of each sample. In order to understand the repeatability of plasma treatment, standard deviation was also calculated in percentage.

In order to determine how long the improvement of adhesion properties can be offset depending on the storage time between primer and plasma pre-treatment and the bonding of specimens, the pre-treated specimens were exposed to the laboratory environment for the storage times of 4, 7 and 15 days. As a measure of the durability of the primer and plasma treatments, the bond shear strength immediately after bonding was compared with that after three different storage times in a laboratory.

3 Results and discussion

3.1 Effects of pre-treatment on contact angle

Table 2 shows the values of contact angles for untreated, primer treated and plasma treated polyethylene using a power input of 50 W and different treatment times. Each value was measured as soon as the samples were withdrawn from the reactor.

Table 2 Contact angle on polyethylene surfaces

Surface treatment		Contact angle (°)
No treatment		80 ± 3
Primer treatment		83 ± 2
Plasma treatment		
Power input (W)	Time (s)	
50	5	40 ± 5
50	30	40 ± 5
50	60	31 ± 2
50	180	33 ± 2
50	300	35 ± 1
50	600	35 ± 2
100	60	31 ± 3
150	60	<15
200	60	<15

The primer surface pre-treatment does not affect the surface wettability of polyethylene in any way. Indeed, the contact angle remains almost unchanged compared to the untreated one, both being close to 80°, indicating poor wettability.

On the contrary, the application of a plasma discharge, even at a low power input, produces a strong increase in surface wettability, reducing by more than half of the contact angle compared with the untreated surface. Concerning the 50 W treatments, the best result in terms of surface wettability was obtained for both the 60 and 180 s treatments: indeed, considering the uncertainty, the two intervals are overlapping and present the lowest contact angle values.

Figure 1 shows the variation of the demineralised water contact angle values of the low pressure plasma treated polyethylene as a function of treatment time (from 5 to 600 s). Contact angle of untreated and primer treated samples are also reported as a comparison.

As it is easy to observe, the use of short exposure times (less than 60 s) is enough to obtain a significant decrease in contact angle values, which means high wettability of the surface, while longer exposure times do not significantly improve wettability.

This is due to the fact that the main act of the air plasma is surface activation by insertion of polar

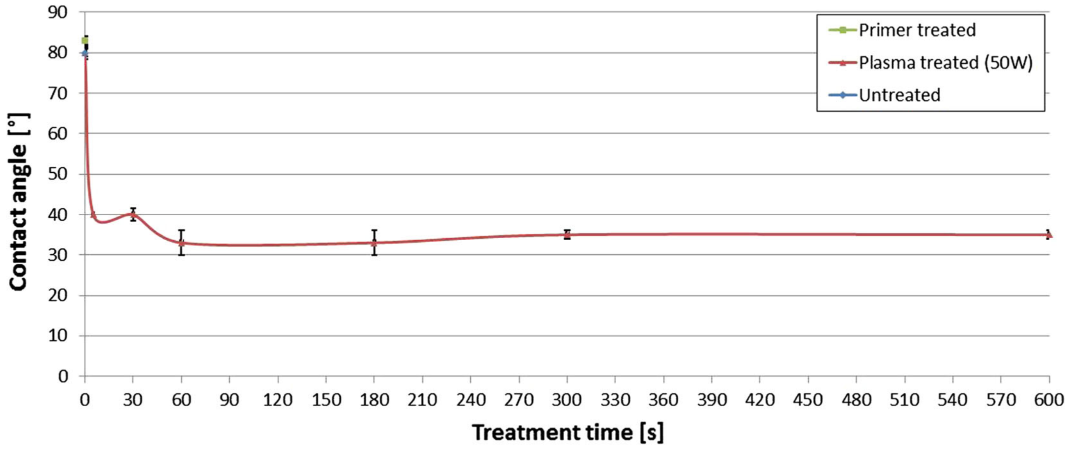

Fig. 1 Variation of contact angle measured on polyethylene surface in terms of treatment time and kind of treatment

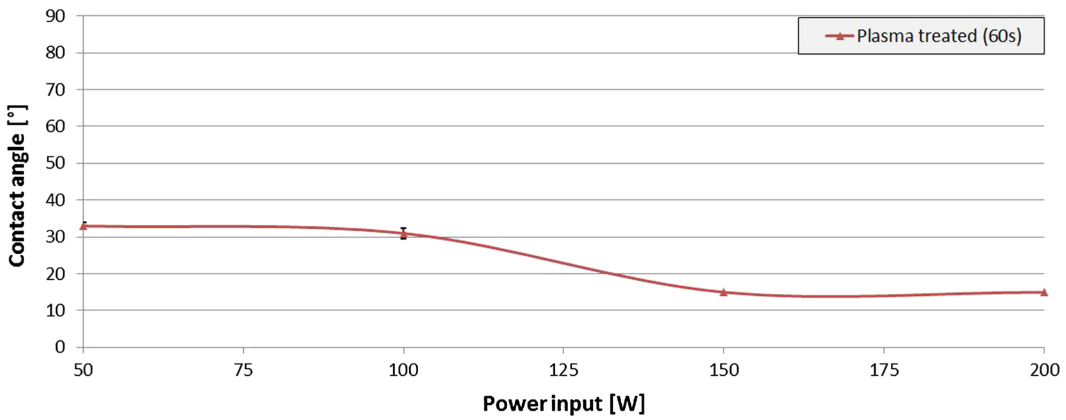

Fig. 2 Variation of contact angle measured on polyethylene surface in terms of plasma power input

species. This process occurs during the first seconds of the plasma treatment when the free radicals produced by the action of the plasma gas present high instability and reactivity [29].

It was therefore also decided to investigate the effect of higher power inputs on surface energy. Figure 2 shows the results of the test. Likewise in this case, the angle values were obtained as the average of three different measurements.

It is useful to observe that treatment for power inputs equal to or greater than 150 W, the surface energy of the substrates raised an almost perfect wettability, indeed the drop is completely "spread" on the specimen surface: the contact angle in these cases was lower than 15° and the drop deposited formed a liquid film. Figure 3 shows two images of the drop deposited on polyethylene only degreased (Fig. 3a) and treated at 100 W for 60 s (Fig. 3b).

The effect of plasma power on metallic substrates was discussed by Lee et al. [21], Sorrentino and Carrino [22] and Tang et al. [23], with results very similar to those reported in this study for polyethylene. The plasma power is linked with the potential to produce the functionalized layer on the surface. Because of the hydrophilicity of the functional group constituting the layer, the drops of water are easily absorbed into substrate surface and contact angle decreases. On the other hand, if the plasma treatment power is too high, the surface will be over-etched, its uniformity will decline and might also be damaged by heat generated during the plasma treatment.

From the results, the surface wettability improved even using short plasma treatment time and using a high power level it is possible to minimize contact angle values.

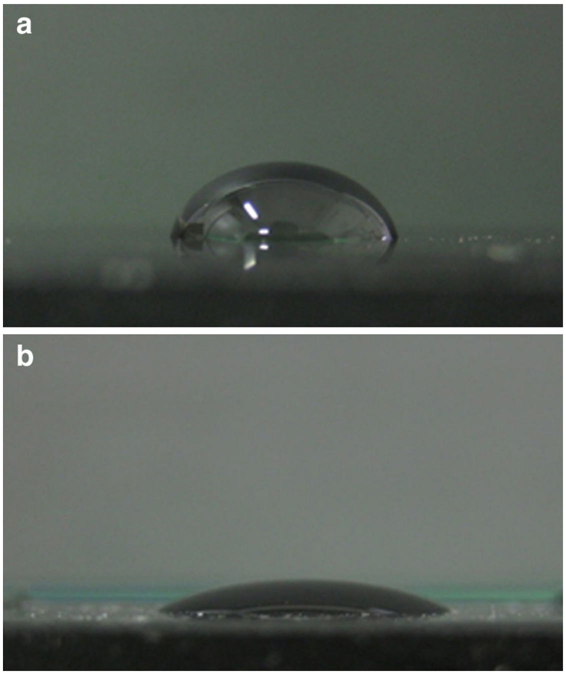

Fig. 3 Polyethylene only degreased (**a**) and treated for 60 s at a power input of 100 W (**b**)

3.2 Effects of plasma pre-treatments on lap-shear strength

Adhesive joints between two polyethylene substrates were realized, comparing primer and plasma treated surfaces with untreated ones. Single lap shear tests were conducted as mechanical characterization. Figure 4 reports shear strength of the joints in terms of plasma treatment time, the power input being fixed. Each point of the curve represents the average strength of five joints with the corresponding time-power setup. For each of those points, the standard deviation is shown.

The graph also includes two horizontal lines representing the average value of shear strength of primer treated and untreated joints.

The result shows that without surface preparation the joints presented very low shear strength, but it increased three times using an appropriate primer. Polyolefins, such as polyethylene, could be primed for adhesion to cyanoacrylates by certain chemical compounds, like the aliphatic amine contained in Loctite® 770 ™, normally considered to be activators for cyanoacrylate polymerization. Another essential effect of the primer for adhesion properties improvement is that its solvents wet-out and swell the polyolefin. This facilitates interpenetration of the low viscosity cyanoacrylate resin in the top-most layer of the substrate [4].

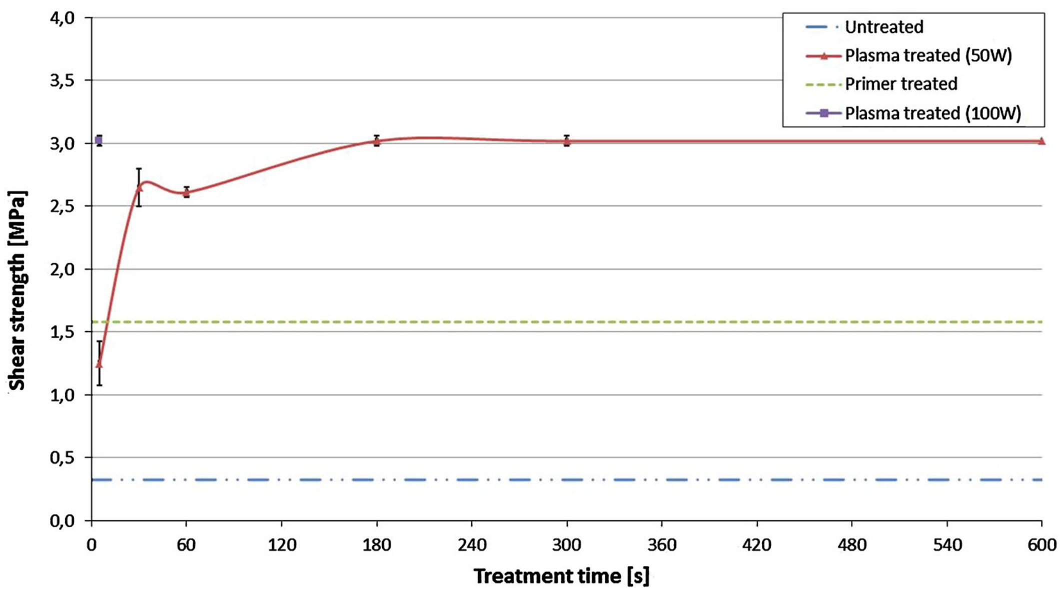

Fig. 4 Comparison between shear strength of plasma treated, primer treated and untreated samples

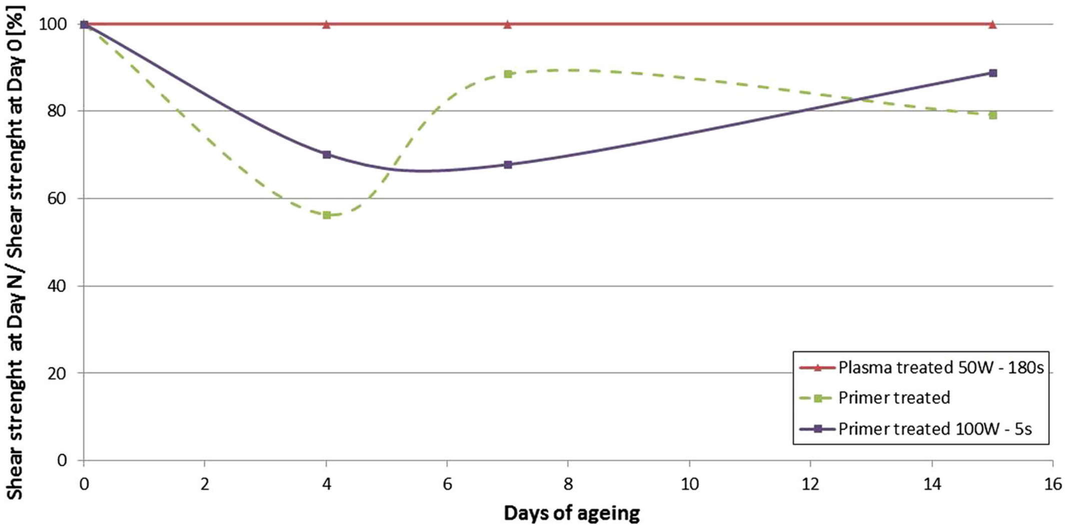

Fig. 5 Time-dependence of bond strength on exposure time for plasma and primer treated samples

A real improvement in mechanical properties is given by the plasma treatment: the results of lap shear tests are evidently satisfactory and in total agreement with those obtained for surface energy evaluation. It can be noticed that strength increases with treatment time and a short exposure under a 50 W plasma discharge, is enough to exceed the shear strength obtained with primer treated specimens. It should also be pointed out that, the asymptotic value corresponding to a plasma treatment of 180 s or more (3 MPa), is not determined by joint failure, but by the substrates' strength, which deformed permanently and experienced considerable elongation.

Concerning the effect of plasma power input, it is easy to observe that increasing this parameter a very short time is sufficient, equal to 5 s, to reach the load that produces the macroscopic deformation of the substrates. This set up is represented on the diagram in Fig. 4 by the point in the upper left.

From these results it is clear that plasma power input and treatment time significantly affected the mechanical properties of adhesive bonding joints. Finding the optimal combination of these parameters it is possible to increase the strength of untreated joints ten times and the primer treated ones twice.

3.3 Ageing of surface treatments

Figure 5 compares the time-dependence of bond strength on exposure time of pre-treated specimens to laboratory air for primer and for plasma pre-treated polyethylene samples. Two sets of plasma treatment parameters were chosen: 180 s at 50 W and 5 s at 100 W, which represent the best results in terms of shear strength. Each point of the curve represents the ratio between the average strength of the joints bonded on the N-th day of plasma treatment ageing and the average strength of the joints bonded without any intermediate time.

It can be observed that the joint realized with the substrates treated with the plasma setup 50 W—180 s keep the strength unchanged, despite the exposition to laboratory environment. Also the 100 W—5 s setup gave quite satisfactory results, especially for an high number of days of ageing, even though not remaining at 100 % of its performance. Other authors, such Mühlan et al. [30], described the excellent behaviour to ageing time of the plasma treatment using a polyurethanic adhesive on polypropylene surfaces, even for longer exposure period, and the tests reported in this paper confirm the good suitability of this treatment for different polymeric substrates and adhesives.

Also the primer treatment gave good outcomes under laboratory ageing. However, unlike the plasma treatment at 50 W, the results do not show a defined trend. Indeed, a short ageing time seems to give the worst results in terms of lap shear strength.

4 Conclusions

This study focused on the effect of cold plasma treatment on polyethylene surfaces. The improvement in adhesion properties of plasma treated polymers has been described in terms of wettability, evaluated by contact angle measurement, and lap shear strength of the adhesive bonded joints realized using treated surfaces. The results were also compared with untreated substrates and a conventional primer treatment.

The results have primarily emphasized how critical the surface preparation is to obtain good joints. This is particularly true for plastic substrates, especially polyolefins, due to their low surface energy and adhesion properties, for which they require a surface treatment that goes beyond simple degreasing with a solvent. This could be stated observing the results of the wettability tests: polyethylene has a very poor wettability, indicated by contact angle values near to ninety degrees. The plasma treatment has proven to be extremely effective, the surface wettability of polyethylene has increased significantly even at low power inputs and for short times.

Concerning the lap shear strength of the joints realized treating the substrates at different parameter set-up, the plasma treatment resulted I a successful solution: the combinations 180 s—50 W and 5 s—100 W led to a permanent deformation and considerable elongation of substrate material and not to a failure of the bonding area, giving also better results compared to primer treated surfaces.

From the economic point of view it could be concluded that shorter exposure time at higher power represents the most effective solution. On the other hand, rom the investigation on ageing of the surface treatment, it could be stated that longer exposure times at low power input give a more long-lasting treatment.

The activation by plasma represents a fast and eco-friendly technology and also develops an effect on polyethylene remaining almost constant and repeatable for long periods, which allows not only the storage but also transportation of the materials.

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References

1. Hayat F (2011) Comparing properties of adhesive bonding, resistance spot welding and adhesive weld bonding of coated and uncoated DP 600 steel. Int J Iron Steel Res 18(9):70–78
2. Sadowski T, Kneć M, Golewski P (2010) Experimental investigations and numerical modelling of steel adhesive joints reinforced by rivets. Int J Adhes Adhes 30:338–346
3. Da Silva LFM, Pirondi A, Ochsner A (2011) Hybrid adhesive joints. Springer, Heidelberg
4. Petrie EM (2000) Handbook of adhesives and sealants. McGraw-Hill, New York
5. Baldan A (2004) Review adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: adhesives, adhesion theories and surface pretreatment. J Mater Sci 39:1–49
6. Underhill PR, DuQuesnay DL (2009) The dependence of the fatigue life of adhesive joints on surface preparation. Int J Adhes Adhes 26:62–66
7. ASTM D2093–03 (2003) Standard practice for preparation of surfaces of plastics prior to adhesive bonding
8. Wegman RF, Van Twisk J (2013) Surface preparation techniques for adhesive bonding. Elsevier, Amsterdam
9. Iqbal HMS, Bhowmik S, Benedictus R (2010) Surface modification of high performance polymers by atmospheric pressure plasma and failure mechanism of adhesive bonded joints. Int J Adhes Adhes 30:418–424
10. Encinas N, Abenojar J, Martínez MA (2012) Development of improved polypropylene adhesive bonding by abrasion and atmospheric plasma surface modifications. Int J Adhes Adhes 33:1–6
11. Schulz U, Munzert P, Kaiser N (2001) Surface modification of PMMA by DC glow discharge and microwave plasma treatment for the improvement of coating adhesion. Surf Coat Technol 142:507–511
12. Zhenga Z, Rena L, Fenga W, Zhaia Z, Wanga Y (2012) Surface characterization of polyethylene terephthalate films treated by ammonia low-temperature plasma. Appl Surf Sci 258:7207–7212
13. Cioffi MOH, Voorwald HJC, Hein LRC, Ambrosio L (2005) Effect of cold plasma treatment on mechanical properties of PET/PMMA composites. Composites A 36:615–623
14. Baumgärtner KM, Schneider J, Schulz A, Feichtinger J, Walker M (2001) Short-time plasma pre-treatment of polytetrafluoroethylene for improved adhesion. Surf Coat Technol 142:501–506
15. Abenojar J, Torregrosa-Coque R, Martínez MA, Martín-Martínez JM (2009) Surface modifications of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS) copolymer by treatment with atmospheric plasma. Surf Coat Technol 203:2173–2180
16. Carrino L, Moroni G, Polini W (2002) Cold plasma treatment of polypropylene surface: a study on wettability and adhesion. J Mater Process Technol 121:373–382
17. Park J, Won-tae J, Paek K, Kim Y, Choi Y, Kim J, Hwang Y (2003) Pre-treatments of polymers by atmospheric pressure ejected plasma for adhesion improvement. Surf Coat Technol 174:547–552
18. Ku JH, Jung IH, Rhee KY, Park SJ (2013) Atmospheric pressure plasma treatment of polypropylene to improve the bonding strength of polypropylene/aluminum composites. Composites B 45:1282–1287
19. Lehocky M, Drnovska H, Lapčíková B, Barros-Timmons AM, Trindade T, Zembala M, Lapčík L Jr (2003) Plasma surface modification of polyethylene. Colloids Surf A 222:125–131

20. Ting JAS, Rosario LMD, Lacdan MCC, Lee HV Jr, De Vero CJ, Ramos HJ, Tumlos RB (2013) Enhanced adhesion of epoxy-bonded steel surfaces using O_2/Ar microwave plasma treatment. Int J Adhes Adhes 40:64–69
21. Lee CJ, Lee SK, Ko DC, Kim DJ, Kim BM (2009) Evaluation of surface and bonding properties of cold rolled steel sheet pretreated by Ar/O_2 atmospheric pressure plasma at room temperature. J Mater Process Technol 209:4769–4775
22. Sorrentino L, Carrino L (2009) Influence of process parameters of oxygen cold plasma treatment on wettability ageing time of 2024 aluminium alloy. Int J Adhes Adhes 29:136–143
23. Tang S, Kwon OJ, Lu N, Choi HS (2005) Surface characteristics of AISI 304L stainless steel after an atmospheric pressure plasma treatment. Surf Coat Technol 195:298–306
24. Choi DM, Park CK, Cho K, Park CE (1997) Adhesion improvement by plasma treatment of polyethylene. Polymer 38:6243–6249
25. Petasch W, Räuchle E, Walker M, Eisner P (1995) Improvement of the adhesion of low-energy polymers by a short-time plasma treatment. Surf Coat Technol 74:682–688
26. Fombuena V, Balart J, Boronat T, Sánchez-Nácher L, Garcia-Sanoguera D (2013) Improving mechanical performance of thermoplastic adhesion joints by atmospheric plasma. Mater Des 47:49–56
27. Tanarro I, Herrero VJ, Carrasco E, Jiménez-Redondo M (2011) Cold plasma chemistry and diagnostics. Vacuum 85:1120–1124
28. Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P (2006) Atmospheric pressure plasmas: a review. Spectrochim Acta 61:2–30
29. Sanchis R, Fenollar O, Garcìa D, Sánchez L, Balart R (2008) Improved adhesion of LDPE films to polyolefin foams for automotive industry using low-pressure plasma. Int J Adhes Adhes 28:445–451
30. Mühlhan C, Weidner ST, Friedrich J, Nowack H (1999) Improvement of bonding properties of polypropylene by low pressure plasma treatment. Surf Coat Technol 116:783–787
31. Loctite (2013) Technical data sheet Loctite® 401™
32. Loctite (2013) Technical data sheet Loctite® 770™
33. ASTM D3163–01 (2008). Standard test method for determining strength of adhesively bonded rigid plastic lap-shear joints in shear by tension loading