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ATMOSPHERIC PLASMA TREATMENT OF POLYETHYLENE SUBSTRATES FOR IMPROVED MECHANICAL PERFORMANCE OF ADHESION JOINTS

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Abstract: *Most industrial polymers and composites have low surface free energy and lack of polar functional groups on their surface, resulting in a class of materials with poor adhesion properties. Currently used chemical or physical processes that have a number of drawbacks as they use products which harm the environment. An alternative to these processes are the treatments using plasma technologies. The equipment of plasma was situated in a stand, making it possible to modify the distance between sample and nozzle. In addition is possible to vary the feed speed of the sample with an adjustable speed drive. Therefore are analyzed the chemical and physical processes that occur on the surface of polyethylene that increase its adhesive properties changing the feed speed and distance between sample and nozzle. The adhesive properties were evaluated by peeling tests. The results show that at low speeds and distances the polar molecules are grafted in the surface of polyethylene giving a higher superficial modification.*

Key words: *polyethylene, wettability, plasma treatment, peeling test, adhesion joints.*

1. Introduction

Polyethylene is one of the world's most used thermoplastics. This is due to its good physical properties, low density, chemical and mechanical resistance, in addition to the economic competitiveness of its industrial production [5].

However, like most polyolefins, this material has certain limitations in industries which require good adhesion of polymers with another kind of substrate or adhesion of polyolefin/polyolefin for example. These sectors demand an improvement in the adhesive properties of polyethylene. Polyethylene, due to its apolar nature, has a low wettability, which induces poor adhesive bonding. Over the past years several physical and chemical technologies have been used to modify the surface properties of polyethylene. An alternative to these processes, is to use plasma-based technologies to modify its surface. In the present study an atmospheric plasma system are used for surface modification of polyethylene. This process is able to increase the surface energy, and therefore their adhesive properties. The surface energy calculation was performed by measuring the contact angle using different liquids.

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The mechanisms of action and physical and chemical changes of the surface have been evaluated. The adhesive properties of atmospheric plasma-treated substrates at different hights and speeds were measured passing through the testing of *T*-peel [8].

2. Experimental

2.1. Materials

Alcudia LDPE PE-019 polyethylene was used as testing material, characterized by its low density and supplied by Repsol YPF.

The liquids used to measure the contact angle have a different polarity in order to determine the polar and dispersive component of surface energy. The used liquids were: Diiodometano: 99% stabilized provided by Acros Organics, distilled water, formamide for analysis (reagent grade) ACS, Scharlau Chemie SA and glycerol 99% extra pure E442 from Scharlau Chemie SA.

The used adhesive was Gray Polyurethane 801 supplied by Kefren S. A. Alicante.

2.2. Atmospheric plasma and sample preparation

The LDPE was previously injected in the form of rectangular plates of size 160×60×2 mm^3. After, the samples were cut small test pieces, with dimensions of 40×15×2 mm^3 to be modified by atmospheric plasma.

A Plasma Jet RD1004 apparatus, provided by "Plasmatreat GmbH", Germany, was used to carry out the surface treatments.

After cutting and washing with distilled water, a speed and distance between nozzle and sample treatment, were selected. We have evaluated ten speeds between 100 and 1000 mm/s, at intervals of 100 mm/s. Treatment distances were 6, 10, 14 and 20 mm. Immediately after the passage of the sample under the action of atmospheric plasma contact angles were measured with the four different liquids.

2.3. Contact angle measurements and surface energies estimation

Static contact angle measurements of the plasma treated samples were carried out at room temperature on a Easydrop Standard, FM140 110/220 V, 50/60 Hz goniometer of KRÜSS, using four different test liquids. Five different drops were measured. In each drop, ten results were obtained and the average was calculated. The average of the five drops was set to be the final value. The maximum error in the contact angle measurements did not exceed 3%. Surface energies were calculated using the Owens-Wend method [1]. In this method, it is possible to determine the solid surface energy (γ) as the sum of polar (γ_p) and dispersive (γ_d) contribution using at least two different test liquids [17], [19]:

$$\gamma_1 \frac{1+\cos(\theta)}{2(\gamma_l^d)^{1/2}} = (\gamma_s^p)^{1/2}\left[\frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}}\right] + \\ + (\gamma_s^d)^{1/2}. \tag{1}$$

Constant values for the four test liquids used for contact angle measurements are shown in the Table 1.

Components of surface energy of different liquids used Table 1

Contact liquid	**γ_s^d [mJ/m^2]**	**γ_s^d [mJ/m^2]**	**γ_s [mJ/m^2]**
Water	22.0	50.2	72.2
Glycerol	34.0	30.0	64.0
Diiodomethane	48.5	2.3	50.8
Formamide	32.3	26.0	58.3

2.4. *T*-peel test and surface morphology study.

To verify the improvement in adhesion properties after the atmospheric plasma process, the *T*-peel tests were conducted on treated samples at different speeds, and different distances between the source plasma and the polymer substrate. Samples were tested after atmospheric plasma treatment and after the adhesion of two samples, exceeded 24 hours of curing the adhesive. In tensile test the speed of opening of the clamps, is provided by normative, 300 mm/s. The equipment used for *T*-peel test was an electromechanical machine drive Elib 50 (SAE Ibertest, Madrid, Spain).

The morphology of the surface after *T*-peel test for the LDPE plates treated with atmospheric plasma was evaluated through scanning electron microscopy (SEM), provided by FEI Phenom model FEI Company, Eindhoven, The Netherlands.

The analysis of X-ray photoelectron spectroscopy (XPS) of various LDPE treated samples were carried out in a VG-Microtech Multilab.

3. Results and Discussion

3.1. Changes in surface wettability

Figure 1 shows the results of contact angle obtained in a sample treated at 6 mm distance and different speeds. This figure shows that, at lower speed, the value of contact angles are lower, mainly due to the higher exposure time to plasma and, consequently, there is an increasing surface activation.

These results should be compared with the angles obtained from a sample of untreated LDPE. The angle value of water is 100.05°, the value of glycerol is 86.72°, the diiodometano is 62º and 80.96º for the formamide. These values are characteristics of a substrate with high hidrofobicity [12], [14].

In the case, at a speed of 100 mm/s, where the superficial modifications is higher, the decrease of the contact values (using water) is 80%, if compared to the untreated sample, which shows the effectiveness of plasma to modify the hidrofobicity of polyethylene. Glycerol shows a decrease of about 70%, diiodomethane to almost 40% and with formamide, a decrease almost 90%.

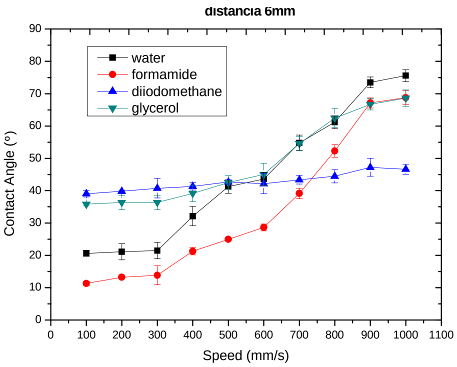

Fig. 1. *Evolution of contact angle on a sample treated with 6 mm apart and at different speeds*

With previous results we have calculated the surface energy of the sample. The results are shown in Table 2. The surface energy results from all tests are represented in a graph in a three dimensional plot (Figure 2) where you can see the influence of speed and distance from treatment [21].

Notably, at low speeds and distances is the polar component the greatest contribution to increase the surface energy. This behaviour is most probably due to the fact that the plasma induces polar molecules in the polymer surface. These polar molecules are activated species present in the air, because the activated gas in plasma is air. The increase in polar contribution decreases the hydrophobicity and therefore the wettability increases. These results are in agreement with XPS analysis performed [13], [18], [22]. Table 3 shows that the amount of oxygen and nitrogen is higher at low speeds and distances, as a result of the increased integration of polar molecules.

At low distances and speeds, the atomic percentage of oxygen is of 29%, while the percentage of nitrogen, is only present in the most aggressive conditions, with a value of about 2% at [2], [23].

Table 2

Values of surface energy with polar and dispersive components in sample treated at 6 mm

Speed [mm/s]	γ_s **[mJ·m^{-2}]**	γ_s^p **[mJ·m^{-2}]**	γ_s^d **[mJ·m^{-2}]**
100	62.89	41.43	21.46
200	62.63	41.50	21.13
300	62.18	41.61	20.58
400	59.52	38.19	21.33
500	53.64	30.07	23.58
600	51.12	28.06	23.06
700	43.58	19.83	23.74
800	40.30	15.35	24.95
900	34.65	8.22	26.43
1000	34.09	6.94	21.46

3.2. T-peel test

The improvement in wettability, provides a considerable increase of surface energy, which in the starting polymeric materials, is around 27.4 mJ·m^{-2} while in the samples treated in a more aggressive conditions, this value reaches values above 64 mJ·m^{-2}.

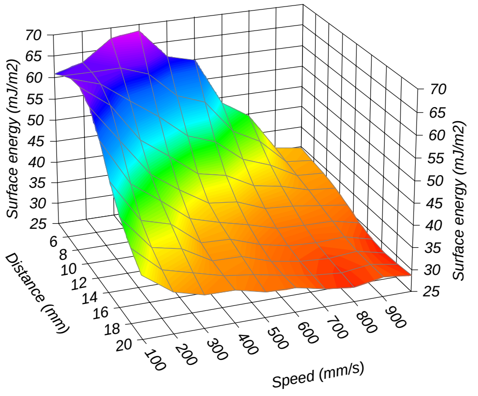

Fig. 2. *Graph of the variation in global surface energy* (γ_s) *seen in 3D*

In this section the *T*-peel test of the samples evaluated, for samples-treated for conditions 100, 300, 700 and 1000 mm/s and different distances: 6, 10, 14 and 20 mm. The main goal is to quantify the mechanical response of bonded joints for the different conditions of atmospheric plasma treatment using a peel test "*T*" between LDPE substrates.

It should be mentioned that previous studies have concluded that, the bond force obtained was virtually zero in two substrates of untreated LDPE.

Figure 3 shows a three-dimensional plot, where the maximum force values obtained for *T*-peel tests are correlated with all conditions studied. The results for each type of treatment result from an average performance of five different assays.

Surface compositions (*atomic %*) *obtained by XPS* Table 3

D **[mm]**	***S*** **[mm s^{-1}]**	**% atomic C**	**% atomic O**	**% atomic N**
untreated	untreated	71.34	15.65	0
6	100	69.1	28.9	2.0
	300	72.0	26.6	1.3
	700	78.8	20.8	0.4
	1000	83.1	16.9	0.0
20	100	70.4	29.6	0.0
	300	72.2	27.8	0.0
	700	77.4	22.6	0.0
	1000	71.0	29.0	0.0

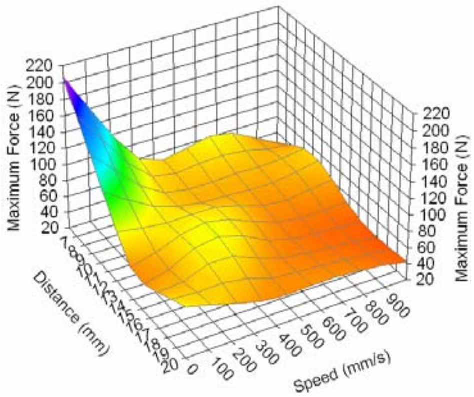

Fig. 3. *Variation of maximum force*

The results show values higher than 195 N for a sample treated at 100 mm/s and 6 mm of distance. There was a trend to decrease the maximum peel force as the processing speed increases. This trend is confirmed with the results obtained with wettability. Simultaneously, at lower processing speeds, the wettability of the samples increases. This increase in wettability of the samples, increases the mechanical properties of adhesive bonds [6], [20]. This is due to the plasma treatment increases surface roughness, witch improves the adhesive properties [10], [15].

3.3. Study of surface morphology

This section is a study of the morphology of the samples of *T*-peel test treated at different distances and speeds. This will be able to draw conclusions about the direct correlation between the morphological appearance of the surface of polyurethane and the mechanical properties obtained [4].

At low speeds and distances, the morphology is regular, with all surfaces with the same morphology, resulting in a cohesive failure of adhesive provides good adhesion of the samples. While at high treatments conditions is more irregular, producing cohesive fracture zones and areas of non-adhesive grip. In these conditions the adhesive does not adhere to the substrate, leaving bare spots that do not offer resistance to the separation between the adhesive and the substrates. Moreover, the sample of untreated LDPE substrate is completely even as a reason for low grip between the two polymeric substrates, thus providing null mechanical strength [9], [11].

SEM revealed three types of morphology: characteristic of untreated and treated samples at high speeds and distances, another image typical at intermediate distances and speeds, where the prevailing slip adhesive, and finally imaging features of good adhesion for cohesive failure, the main mechanism of action of samples treated at low speeds and distances [7].

The left micrograph shows that the morphology of the fracture surface is characterized as completely smooth, uniform and homogeneous, with the presence of adhesive on one side of the union, indicative of the lack of adhesion to the surface LDPE [3].

In the middle photo, in a sample treated in intermediate conditions of speed and distance, one can see polyurethane glides. These areas have a formation of waves indicative of certain adhesive plastic deformation before rupture of the union, because it is an elastomeric adhesive nature [16].

The micrograph on the right are pictures of typical morphology in the presence of “round holes” that belong to a type of cohesive failure of the adhesive, indicating a good bonding process. The failure mechanism of the union takes place through the adhesive so that the internal structure is visible on the fracture surface after the peel test. This type of morphology is present wholly or partly in the samples with atmospheric plasma treatment under optimal conditions: low distance substrate/nozzle and low flow rate.

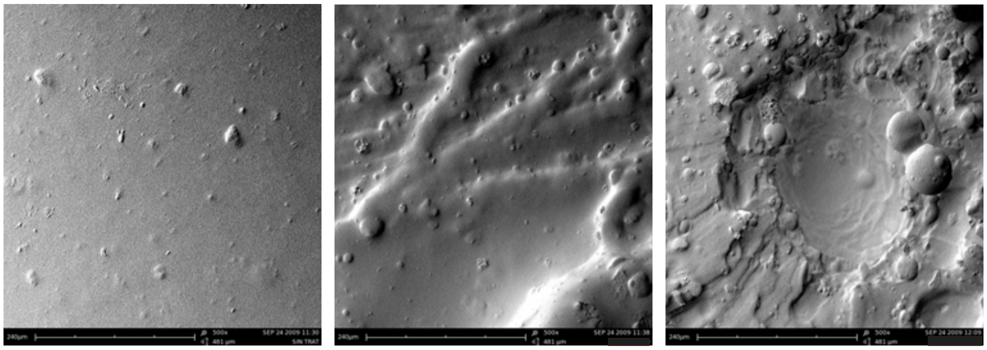

Fig. 4. *Images at 500 times of morphological aspect of untreated sample* (*left*), *one treated at speeds and distances intermediate* (*middle*) *and treated under more aggressive conditions* (*right*)

4. Conclusions

Atmospheric plasma treatment greatly improves the wettability of the surface of LDPE film, results corroborated by a significant reduction in static contact angles. The initial values of surface energy, about 27 $mJ \cdot m^{-2}$ are increased to values close to 65 $mJ \cdot m^{-2}$ after treatment at low speeds and distances.

The values of surface energy, it is worth noting the increase in polar contribution (γ_s^p) which is indicative that one of the main mechanisms of action of plasma surface activation is the insertion of polar groups. Using the XPS analysis is found a considerable increase in the oxygen content at the surface (up to values around 30% atomic for a sample treated at 6 mm apart and 100 mm/s speed) which indicates that the functionalization occurs basically by insertion of different groups containing oxygen atoms.

The maximum force required to separate two substrates treated LDPE increases to values higher than 195N. Changes in surface topography due to the action of different conditions of plasma can be seen qualitatively with the use of scanning electron microscopy (SEM) showing a clear change in surface roughness.

Acknowledgements

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