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THE EFFECT OF ATMOSPHERIC DBD PLASMA ON SURFACE ENERGY AND SHEAR STRENGTH OF ADHESIVELY BONDED POLYMER

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Abstract

Virgin and surface treated polymers are often used in food-processing and packaging industry. Atmospheric cold plasma treatment can effectively modify the adhesive behaviour of the surfaces. An extruded (smooth) surface of PA6 E and UHMW-PE HD1000 have been treated by DBD plasma under air atmosphere conditions. The major objectives of the present study are exploring the effect of DBD plasma on the surface energy and adhesive bonding capability of the polymer. Where the surface energy has calculated, based on Owens-Wendt method and the adhesive (lap-shear) test carried out DIN EN 1465 standard with applying different adhesive types. The results expose that the DBD plasma treatment enhances the adhesive bonding capability due to increased surface energy and modified the topography and the chemical composition of the surface. However, PA6 E shows higher tensile shear strength compared to UHMW-PE HD1000 because of the higher polarity of PA6 E after treatment.

Keywords

DBD cold plasma treatment, surface energy, wettability, shear strength, polymer adhesive bonding

1. Introduction

Nonpolar material and polymers (in particular) have low surface energy thus low adhesion force. A hydrophilic surface is required to obtain adequate adhesion to other material types. On the other hand, the superhydrophobic surface is required for several applications [1]. The development in the testing of sticking technologies of machine parts made of engineering plastics comes into the foreground rather continually [2]. Vehicle industry is a good example of importance to explore quick high strengths and elastic component contacts [3], this made the surface treatment required to promote surface properties. Many different methods have been developed for polymer modification, such as chemical vapor deposition, soft lithographic imprinting, sol–gel method, etc. [1]. However, there are many current and emerging wetting and adhesion issues which require an additional surface processing to enhance interfacial surface properties [4]. Plasma treatment has become the best method to improve the surface wettability of polymers [5]. Among studies have been extensively investigated low-pressure plasma techniques (plasma immersion ion implantation) and their effects on the surface modification of various polymers [6, 7]. Recently, atmospheric-pressure plasma has been rising interest to use for surface modification of polymeric materials instead of low-pressure plasma in the academic research and industrial applications, due to its vacuum less system, operable under atmospheric pressure and its effects of ablation crosslinking and activation.

In the present study, two commercial polymers most commonly used in the industrial, agricultural and medical applications have been selected: Polyamide 6 Extruded (PA 6 E) and Ultra High Molecular Weight Polyethylene High Density 1000 (UHMW-PE HD1000).

In literature, the results showed the that atmospheric cold plasma treatment in a low-pressure increase the surface energy of PE and they found that plasma improves the using of PE in the medical applications [8] and it enhances the shear strength of adhesive bonding also [9]. In parallel, PA 6 illustrated better surface energy and adhesive bonding over plasma treatment [10].

The main aim is finding a correlation between pristine and treated surface properties from the point of surface energy, thus adhesion and shear strength of adhesive bonding for polymer/polymer and polymer/ steel pairs for the selected polymers.

2. Materials and methods

Materials and preparation

Two types of commercially available engineering polymers (distributed by Quattroplast Ltd., Hungary and produced by Ensinger GmbH, Germany), were used in bulk conditions: Polyamide 6 Extruded or PA6 E grade Docamid-6-E and Ultra High Molecular Weight Polyethylene High Density 1000 or UHMW-PE HD1000 grad Docalene-HD1000. The mechanical properties of the materials are as follows: PA6 E (elastic modulus E = 3300 MPa, tensile strength σ = 79 MPa, glass transition temperature Tg = 45 °C), UHMW-PE HD1000 (elastic modulus E = 680 MPa, tensile strength σ = 22 MPa, Melting temperature= 135 °C). Structural steel (S 235 JR N) was used as counterfaces for the adhesive test, it is one of the most common type of the general-purpose, non-alloy steels with low carbon content (0.17 %). In general, its Rm= 400-500N/mm^2 (Ferroglobus Ltd, Hungary). Different adhesives (Henkel Loctite, Hungary) were applied with bond line (thickness) 0.1 mm: Loctite 406 (Ethyl cyano-Acrylate), Loctite 3035 (Methacrylate-Acrylic), Loctite 9466 (Two-component Epoxy), Loctite 330 (Urethane metacrylate ester- Acrylic) and Loctite 770 (Aliphatic amine-Primer, Cyanoacrylate) as primary activator, detailed technological steps specified and properties of each glue are available in (Technical Data Sheet (TDS) of Loctite) [11]. The polymer applied very smooth (extruded) surfaces. Before testing, the samples were cleaned in an ultrasonic bath with distilled water and 96% ethanol (Reanal, Hungary). The surface energy evaluation samples were prepared in disc-shaped samples with a diameter of 10 mm and thickness of 2 mm. For adhesive test the samples (polymer and steel) were prepared in a rectangular shape with dimensions: 25.4 mm x 100.0 mm x 2.0 mm as shown in Figure 1. The polymer samples were cut from extruded plate.

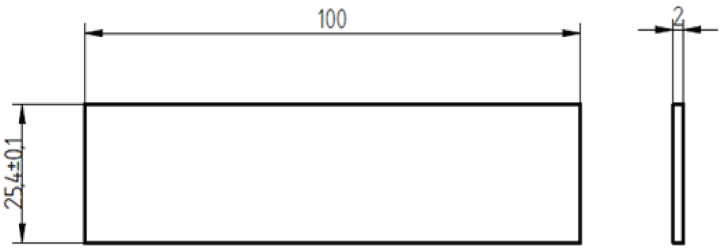


Figure 1. Sample dimensions of adhesive test

Table 1. illustrates the materials and used adhesives (the Loctite made a choice based on Technical Data Sheet (TDS) recommendation) [11].

Table 1. The planning material and adhesives for the bonding test

Bonded materials	Adhesive	Primary activator
PA6E – PA6E	Super glue: Loctite 406	-
	Two-component Epoxy: Loctite 9466	-
	Structural adhesive: Loctite 330	-
PA6E – S235 Steel	Super glue: Loctite 406	-
	Two-component Epoxy: Loctite 9466	-
	Structural adhesive: Loctite 330	-
HD1000-HD1000	Super glue: Loctite 406	Primary: Loctite 770
	Structural adhesive: Loctite 3035	-
HD1000– S235 Steel	Super glue: Loctite 406	Loctite 770 only for HD1000
	Structural adhesive: Loctite 3035	-

Plasma treatment

The atmospheric pressure ambient air plasma was generated by DCSBD plasma source. The principle of DCSBD plasma is based on a coplanar DBD where comb-shape electrodes are embedded in a dielectric. The diffuse plasma is generated in thin 0.3 mm thick flat layer on alumina ceramic which designates the DCSBD to be used especially for treatment of flat surfaces. The DCSBD electrode system was powered by AC HV source of frequency approx. 14 kHz and voltage approx. 20 kV peak-to-peak and the total power in plasma during the experiments was 400 W. The area of generated plasma of DCSBD is 170 cm^2, thus the surface energy density and volume energy density at power of 400 W are approximately 2 W cm^2 and 80 W cm^3, respectively. The DCSBD plasma is described in detail [12]. The plasma treatment was performed in dynamic treatment mode and the distance between the treated polymer surface and DCSBD ceramic was 0.3 mm. The treatment has been done under air atmosphere conditions (T= 23°C, H= 50%), the apparatus shown in Figure 2. The treatment time for each specimen was 1 min.

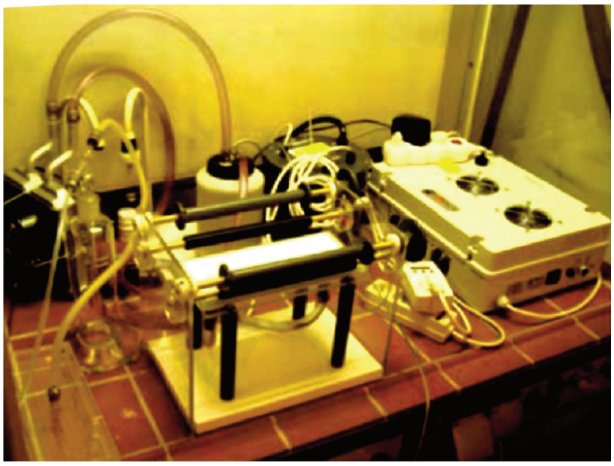


Figure 2. DBD laboratory test equipment used for polymer surface

The marking system of bonded specimens

The different combination of specimens must be distinguished, therefore the following identification has been introduced.

PA6 example:

0_PA6_PA6_406_11_1

- 1. marking: It indicates the condition of the surface (0-pristine surface without plasma treatment, 1-with cold plasma (DBD) treated surface).
- 2. and 3. marking: refer to the conjugate materials.
- 4. marking: refers to the type of adhesive.
- 5. marking: refers to the use of the activator. If 11means activator was used for both surfaces, 00 not one of them, 10, 01 – only one surface.
- 6. marking: refers to the serial numbers of the specimen in the bonding test (from 1 to 5).

Figure 3. SEE System apparatus which used to evaluate the contact angle of polymer

Contact angle measurements

Contact angle measurements were done by the static sessile drop method at 23 °C, with double distilled water and diiodomethane (Sigma–Aldrich, Reagent Plus 99% grade), applying the SEE System apparatus (Ramé hart 100-00) as shown in Figure 3. A Hamilton syringe was used to inject 2 μl droplets. Each result of the contact angle is an average of 5 measurements, performed always on previously non-wetted parts of the samples. The surface energy component calculations based on Owens-Wendt method.

Adhesive test

The tensile test was carried out the ISO 527-1 standard, the overlap joints made according to the DIN EN 1465 standard with a lap-shear test.

The requirements for bonding of the specimens:

- 5 repeated bonding at the same time with a given materials.
- Overlapping has to be 12.5 +_0.1 mm.
- The same normal force (5 N) applied during curing.
- Stick-free bonding-jig to prepare the bond.

The experiments were carried out according to the glue producer's (Henkel Loctite, Hungary) recommendations (Technical Data Sheet – TDS – of Loctite):

- Rough cleaning with water.
- Degreasing of the surfaces with Loctite SF 7063.
- Creating the bonds in the jig.

The two plates were bonded to each other by using the apparatus which made from PTFE to reduce the specimens sticking (knowing, hydrophobic surface of PTFE) as in Figure 4. The specimens prepared adequately on a tensile test machine, according to DIN EN 1465 standard (as mentioned). Although the standard mentions more solutions onto the forming of the specimens, the simple overlap joining was selected. The adhesive test was done within 24 hours after the plasma treatment, To ensure a full effect of DBD plasma. Where the best results of plasma surface modification were performed immediately after treatment, then the surface starts recovering to the reference state after 24 hours [13, 1]. The overlap area of the polymer plates (immediately after plasma treatment) coated with a primary activator (for the glues that have been recommended to use them with primary activator) before adding the adhesives. The glue amounts are 0.035 ml of Loctite 406 and 0.1 ml for the other structural adhesives after the adhesives adding, the plates set up with each other in the apparatus. The test has been repeated 5 times for each polymer and different pairs polymer/polymer and polymer/steel. The tensile test was managed by a (Zwick Roell Z100) tensile machine as shown in Figure 5, with 1.3 m/min pulling speed and 100kN maximum tensile load. The shear strength is equal to the maximum failure force dividing the bonded area.

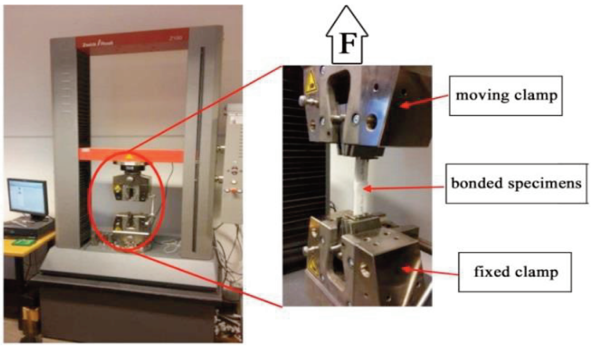


Figure 4. Zwick Roell Z100 tensile test machine

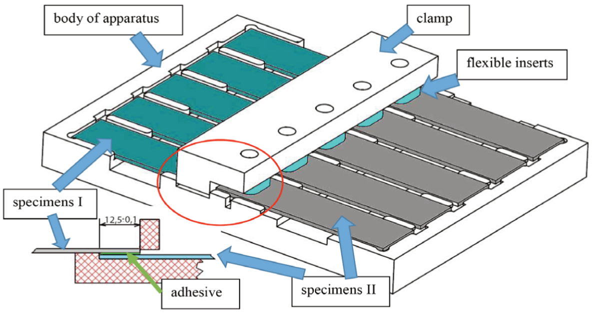
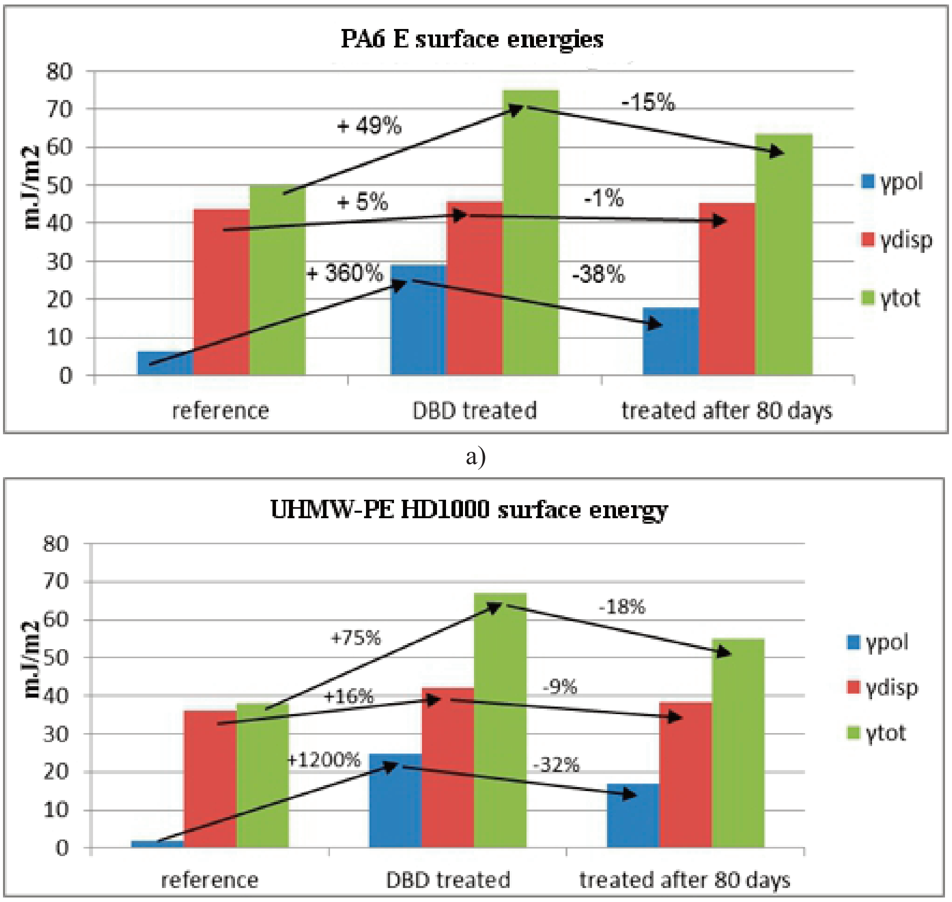


Figure 5. The apparatus which used to bond the pairs

Table 2. Contact angle and surface energy values for pristine and treated surfaces

Sample	Θ_w (deg)	Θ_{CH2I2} (deg)	γ_{pol}(mJ/m^2)	γ_{disp}(mJ/m^2)	γ_{tot}(mJ/m^2)
PA6 untreated	70±7.2	32±2.1	6.3	43.6	50.0
PA6 treated	21±0.5	26±1.5	29.1	45.8	74.9
PE1000 untreated	87±0.4	47±1.9	1.9	36.2	38.1
PE1000 treated	35±2.3	35±5.8	24.7	42.2	67



a)

b)

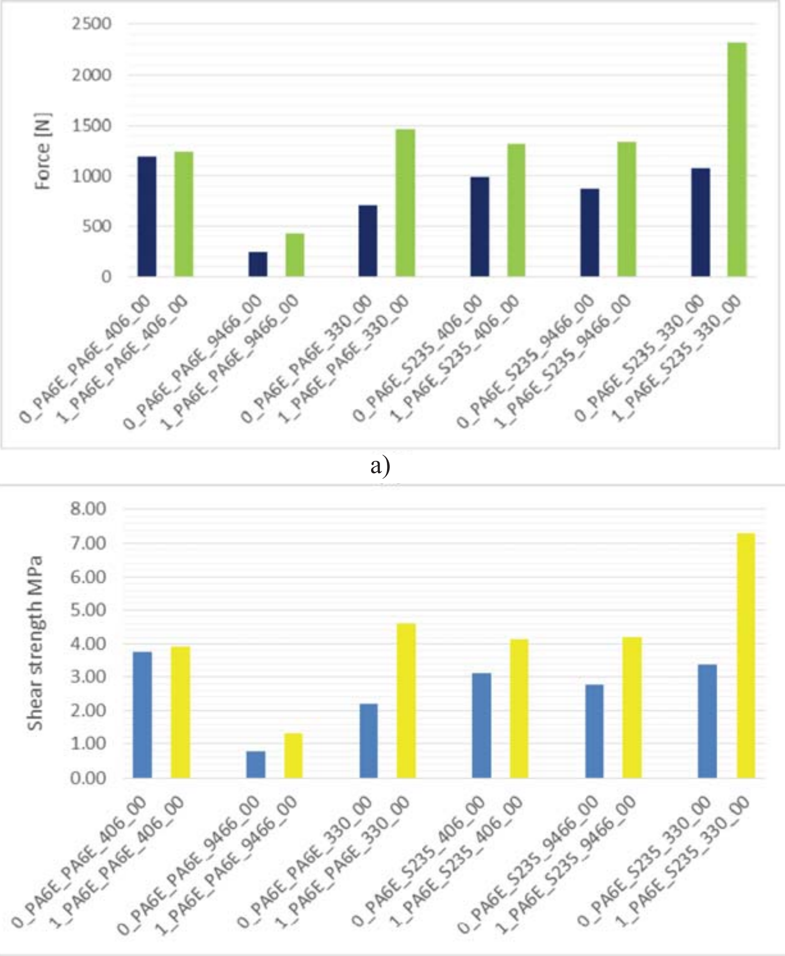
Figure 6. The change in the surface energy values after DBD plasma treatment with 24 hours and 80 days; (a) PA6 E and (b) UHMW-PE HD1000

3. Results and discussion

Surface energy evaluation

The Table 2. Shows the surface contact angle (water and diiodomethane) and surface energy components: polar (Υ_{pol}), dispersive (Υ_{disp}) and total energy(Υ_{tot}) values. Where Figure 6 illustrates the surface energies change for pristine and a DBD plasma treated surface (after 24 hours and 80 days shift time). It can be seen the significant increase of wettability(decrease the contact angles), thus the surface energies. In the case of PA6 E due to DBD plasma treatment, the surface energy increased based on Owens-wendt calculation. Both the polar and disprsive components increased, in particular, the polar component increased 350% more than the original state. The hydrophobic recovery decreases the polar and disprsive components, thus the total surface energy with the function of time, where the polarity decreased 38% and the total energy 15% after 80 days shift time as shown in Figure 6a.

On the other hand, UHMW-PE HD1000 surface energies also increased due to DBD treatment based on Owens-wendt calculation, but the results have Observed that the increasing percent of the surface energy was higher relative to the original surface energy values compared to PA6 E. Where the polar component increased more than 1200% after treatment, within 24 hours. Nonetheless, the action of Hydrophobic recovery decreased the polar and disprsive thus total components with time function, where the polar component and total surface energy expose 32% and 18% less, respectively, after 80 days shift time as shown in Figure 6b. The change in the surface energies with the function of time is very slight (they can be described as negligible) compared to the change due to the effect of DBD plasma treatment.



a)

b)

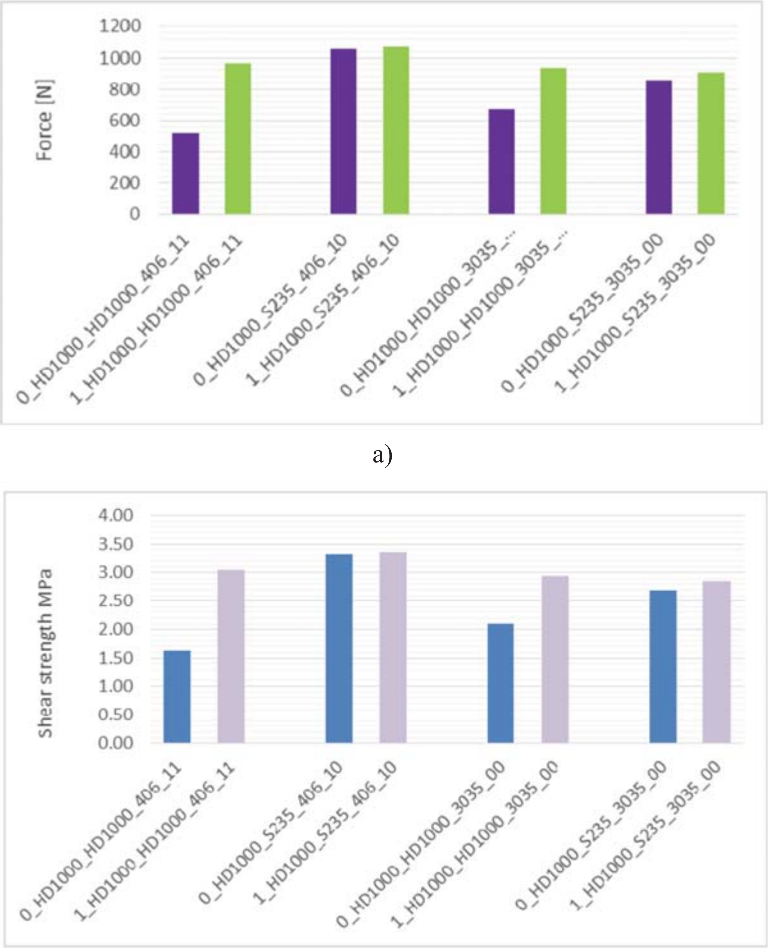
Figure 7. Lap-shear test results of PA6 E (polymer/polymer and polymer/steel pairs) with different adhesives for pristine and DBD plasma treated polymer: (a) average of maximum tensile test and (b) average tensile shear strength

Adhesive tests

The average of maximum force and average shear strength of five repetitions (polymer/polymer and polymer/steel joints) summarized in Figure 7 for PE6 E and Figure 8 for UHMW-PE HD1000. The statistical deviation of PA6 E on the shear strength more low after DBD plasma treatment, whereas slightly reduce due to plasma treatment for UHMW-PE HD1000, irrespective the counterface. In general, the DBD plasma enhances the shear strength, irrespective, adhesive type and counterface as a consequence to increasing the polymer polarity after plasma treatment and modified the topography and the chemical composition. Using different groups of adhesives for each polymer makes the comparison not easy. Generally, PA6 E average shear strength is higher than UHMW-PE HD1000, it is expected, according to the higher polarity which PA6 E was exposed after plasma treatment.

In the case of PA6 E, Loctite 330 shows the highest increasing in the shear strength and Loctite 406 shows the lowest change of shear strength due to plasma treatment. In spite of increased shear strength after plasma treatment for Loctite 406 and Loctite 9466, but they still show comparable shear strength to the pristine surfaces. Where the tensile shear strength of Loctite 406, Loctite 9466 and Loctite 330 increased after plasma treatment: 4%, 70%, and 110% respectively for polymer/polymer joints and: 34%, 53%, and 116% respectively for polymer/steel joint. The failure type change from adhesive failure on one or two surfaces of the pristine surface to cohesive in the adhesive layer failure or adhesive failure on one or two surfaces after plasma treatment of almost 5 repetitions expect polymer/polymer joints with Loctite 406 where kept the same failure type.

In contrast, polymer/polymer joints of UHMW-PE HD1000 expose higher shear strength compared to polymer/steel joints during lap-shear test regardless adhesive type. The increasing in the tensile shear strengths of Loctite 406 and Loctite 3035 joints are 88% and 40% respectively for polymer/polymer joints, and: 1% and 6% respectively for polymer/steel joints. The failure type of 5 repetitions is an adhesive failure on one or two surfaces of the pristine surface and it has remained the same failure type after treatment.



a)

b)

Figure 8. Lap-shear test results of UHMW-PE HD1000 (polymer/polymer and polymer/steel pairs) with different adhesives for pristine and DBD plasma treated polymer: (a) average of maximum tensile test and (b) average tensile shear strength

4. Conclusion

Atmospheric DBD plasma is a very efficient technique to modify the polymer surface. The results of PA6 E and UHMW-PE HD1000 surface modified by DBD plasma under air conditions show:

- Increase the wettability of polymer (decrease the contact angle value) and the surface energy components based on Owens-Wendt method, where the polar component of PA6 E increased more than 350% for PA6 E and 1200% for UHMW-PE HD1000.

- Enhance the average tensile shear strength of adhesively bonded pairs of different couples (polymer/polymer and polymer/steel) and different adhesives during lap-shear test (carried out DIN EN 1465 standard) due to DBD plasma treatment due the surface characterizations modification after plasma treatment. Generally, PA6 E shows higher change in shear strength after plasma treatment because of the high polarity of PA6 E. Regardless pairs type of PA6 E, Loctite 330 shows the highest shear strength, where increased (110-120%) after treatment compared to the pristine surface. However, UHMW-PE HD1000 exposed converse behaviour after plasma treatment, where polymer/polymer pairs showed higher shear strength compared to polymer/steel pairs irrespective the adhesive type. The increase of UHMW-PE HD1000 (polymer/polymer pairs) was (40-90%) compared to the pristine surface.

Acknowledgements

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