OPTIMIZATION OF ATMOSPHERIC PLASMA TREATMENT OF LDPE SHEETS: INFLUENCE ON ADHESIVE PROPERTIES AND AGEING BEHAVIOUR.

Vicent Fombuena, David García-Sanoguera, Lourdes Sánchez-Nácher, Rafael Balart, Teodomiro Boronat.

Instituto de Tecnología de Materiales (ITM), Universidad Politécnica de València (UPV), Campus de Alcoi, Plaza Ferrandiz i Carbonell s/n 03801, Alcoi, Alacant, Spain.

Correspondence to: Vicent Fombuena (Email: vifombor@upvnet.upv.es)

ABSTRACT

One of the major disadvantages of low density polyethylene (LDPE) sheets is their poor adhesive properties. Therefore, LDPE sheets have been treated with atmospheric pressure air plasma (APP) in order to improve their surface properties. In order to simulate the possible conditions in an industrial process, the samples have been treated with two different sample distances (6 and 10 mm) and treatment rates between 100 and 1000 $mm\cdot s^{-1}$. The variation of the surface properties and adhesion characteristics of the sheets were investigated for different aging times after plasma exposure (up to 21 days) using contact angle measurement, atomic force microscopy (AFM), weight loss measurements and shear test. Results show that the treatment increases the polar component (γ_s^p) and these changes improve adhesive properties of the material. After the 21st day, the ageing process causes a decrease of wettability and adhesive properties of the LDPE sheets (up to 60%).

KEY WORDS: Surface modification, ageing, adhesion, polyethylene.

1. INTRODUCTION

The polyolefin thermoplastics are commercially the most common and most economic plastics. One of the more demanded polyolefin is LDPE, this is due to its optimum combination of properties and low cost which are the following: good thermal and chemical resistance, good impact strength, design flexibility and finishing and very good processability. As a consequence it can be processed by thermoplastics processing methods such as injection molding and extrusion [1-5]. However, LDPE has inert surface, non-porous and hydrophobic surface, which results problems in adhesion processes. In these cases it is necessary to carry out a surface treatment in order to increase γ_S and subsequently the adhesion properties [6,7]. An increase in γ_S can be obtained using wet chemical processes, however, these methods are based on the use of aggressive chemicals such as acid or alkalis and they generally could result in some environmental impact [7,8].

In contrast plasma treatment of polymers is an environmentally friendly technique which introduces polar groups and increases surface roughness without affecting the bulk properties [9,10]. Recently, atmospheric plasma treatment is grabbing more attention since it presents high efficiency, it does not need a vacuum system, it can be applied in manufacturing on line processes, and it is scalable to larger areas [11]. APP is easy to be adapted in industrial production lines as an additional material pretreatment stage [12,13].

However, it is also well known that treated surfaces undergo aging, leading to hydrophobic recovery and degradation of hydrophilicity dependent properties over time [14-16]. The mobility of the polymer chains enable the polymer surface to respond to interfacial forces and to adapt their surface chemical structure to their environment [17]. The ageing behavior of plasma treated samples depend on different parameters, such as ageing medium, cross-linking, temperature, humidity, cristallinity, etc., as some authors have already studied [16,18].

In this paper, the influence of sample distance and treatment rate has been studied in detail. The main objective of this study is to achieve an optimization of the working conditions (sample distance and treatment rate), which obtain the greater surface modification, in order to improve the subsequent adhesive processes. Once the optimum work variable has been defined, the ageing conditions have been taken into account, in order to simulate normal conditions of storage in common industrial processes (25ºC and 30 % relativity humidity). The ageing effect was studied over a period of 21 days, emphasizing the first moments after the treatment with APP. This agrees with Borcia et al, that declare that most of the recovery occurs during the first 2 days after the plasma treatment and all further evolutions seem to be less important [19].Contact angle measurements were made in order to study the changes of surface free energy, using the Owens-Wendt method. AFM and weight loss were used in order to study the surface morphology and the etching effect of the surface morphology and the etching effect of the LDPE treated sheets. Shear test was carried out between LDPE-LDPE joint in order to determine the increase of the adhesive properties of the sample. The measurements were made before and after the plasma treatment was carried out in order to compare the obtained results.

Finally, the optimization of the process variable has been achieved allowing its application to industrial processes. In addition the loss hidrophility and adhesion properties during the storage process have been quantified.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

LDPE was provided by Repsol YPF (Madrid, Spain) in pellet form without additives. The LDPE sheet (160x60x2 mm) was obtained by injection molding in recommended conditions. This LDPE is suitable for technical applications. The melting temperature was in the 111-112ºC range, as obtained by DSC analysis.

Two LDPE substrates were joined in shear test, using a Polyurethane Grade 801 supplied by Adhesivos Kefren (Alicante, Spain). Previously, the time of curing of polyurethane was studied and it needed a minimum of 24 hours until the adhesive joint was ready for mechanical characterization.

2.2 APP device

An APP device form Plasma Treat GmbH (Steinhage, Germany) descripted in Figure 1 was used for treating the LDPE sheets. The setup operated at frequency of 17 kHz and at high tension discharge of 20 kV, and it was provided with a rotating torch ending in a nozzle (1900 rpm) through which plasma was spelled. The effects of surface functionalization by insertion of polar groups can be observed if the surface free energy of plasma-treated sheets is calculated. If we take into account that this process can be carried out in a continuous way, an additional variable, the sheet advancing rate, has to be considered in order to evaluate the overall effects of the plasma treatment. For this reason, the samples were placed in a speed-controlled platform, where it is possible to study from 100 to 1000 $mm \cdot s^{-1}$ in treatment rate. It has been studied both 6 and 10 mm distances between the sample and the plasma torch nozzle.

(Figure 1)

2.3 Contact Angle Measurements and γs Calculations.

In order to determine possible changes in the wettability of the LDPE sheets, contact angle was measured both before and after the plasma treatment, and also during the ageing process. Contact angle was measured by Easy Drop Standard goniometer mod. FM 140 supplied by Krüss S. A. (Hamburg, Germany). The maximum error in the contact angle measurement did not exceed ±3%. Four different test liquids were selected for contact angle measurements and γ_s calculations by the Owens-Wendt method. These test liquids were selected to cover a wide range of polar (γ_l^p) and dispersive (γ_l^d) components of the total liquid surface energy (γ_l) [20].

Water:

$(\gamma_l^d) = 22.0$ mJ·m^{-2}, $(\gamma_l^p) = 50.2$ mJ·m^{-2}, $(\gamma_l) = 72.2$ mJ· m^{-2}

Glycerol:

$(\gamma_l^d) = 34.0$ mJ·m^{-2}, $(\gamma_l^p) = 30.0$ mJ·m^{-2}, $(\gamma_l) = 64.0$ mJ· m^{-2}

Diiodomethane:

$(\gamma_l^d) = 48.5$ mJ·m^{-2}, $(\gamma_l^p) = 2.3$ mJ·m^{-2}, $(\gamma_l) = 50.8$ mJ· m^{-2}

Formamide:

$(\gamma_l^d) = 32.3$ mJ·m^{-2}, $(\gamma_l^p) = 26.0$ mJ·m^{-2}, $(\gamma_l) = 58.3$ mJ· m^{-2}

The Owens-Wendt is able to determine both additive contributions of the γ_s, dispersive (due to London type forces) and polar (which accounts for the dipole-dipole and hydrogen bonding interactions [21]. The expression that graphically represents an equation in y= a + bx form is the following:

$$\textbf{(1)}\ \gamma_l \cdot (1+\cos(\theta))/2(\gamma_l^d)^{1/2} = (\gamma_s^p)^{1/2} \cdot \left((\gamma_l^p)^{1/2} / (\gamma_l^d)^{1/2} \right) + (\gamma_s^d)^{1/2}$$

In this equation, the terms with the subscripts *d* and *p* refer to the dispersive and polar component respectively. The contact angle is represented by θ, γ_l is the surface tension of the liquid and γ_s is the surface tension of the solid or surface free energy.

2.4 Morphological Changes

The weight changes as a consequence of the APP modification were determined using a Mettler-Toledo AG 245 balance (Mettler-Toledo, Barcelona, Spain). The LDPE sheets were weighed before and after the exposure to APP. At least, five measurements were taken for each sample and average values were calculated. Moreover, surface topography changes were evaluated with an AFM, using a multimode AFM microscope with a Nanoscope Illa ADCS controller (Veeco Metrology Group, Cambride, UK). A monolithic silicon cantilever Nano World Pointrobe with a constant force of 42 $N \cdot m^{-1}$ and a resonance frequency of 320 Hz was used to work on the tapping mode. Tapping mode AFM imaging technique was used in order to obtain topographic images of the plasma-treated LDPE sheets samples. This mode was preferred to the AFM/LFM (contact mode AFM), because the Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces which may arise after a plasma treatment, and which would distort image data [22]. The area studied is 20x20 μm^2, and all values are included in the range 0-850 nm. These techniques were applied over two sample distances previously studied and for four different treatment rates (100, 300, 700 and 1000 mm·s^{-1}), covering all conditions of possible work.

2.5 Mechanical Characterization and Ageing Conditions

The mechanical characterization of the adhesive joints was carried out using a universal test machine Elib 30 (Ibertest S.A.E, Madrid, Spain), with the objective to find the relationship between a rise of wettability and an improvement of the adhesion properties. Five samples of 25x25 mm^2 in size with different APP conditions were subjected to a shear rate of 50 mm·min^{-1} using the guidelines of the standard ISO 13345. Previously to the specific conditions of treatment with APP, the LDPE sheets were bonded and 24 hours later were tested, as a consequence of the time of curing of polyurethane used. The samples studied were treated in the same conditions than in study of morphological changes.

Later the LDPE sheets were subjected to an aging process in an aging chamber. The selected storage conditions for the aging process were 25ºC and 30 % relativity humidity, simulating normal conditions of storage of pieces in the industry. The mechanical characterization of the adhesive joints was carried out using a universal test machine Elib 30 (Ibertest S.A.E, Madrid, Spain). For the purpose of finding the best conditions of treatment, six conditions of treatment have been studied according to previous studies, concretely 6 and 10 mm for sample distances and 100, 300 and 700 mm·s^{-1} for treatment rates.

3. RESULTS AND DISCUSSION

An evaluation of the γ_s of the pristine LDPE sheet was carried out previous to treatment with APP. None of the test liquids exhibited low contact angles on the original surfaces. The initial contact angle of the film, located around 100.05º, 86.72º, 62.00º, and 80.96º for water, glycerol, diiodomethane and formamide. These high contact angles results are indicative of the non-polar character of the LDPE sheets surface, which is the main cause of the poor wettability and adhesion difficulties to this type of material [23,24]. This contact angle applied in the Owens-Wendt expression give a γ_s of 27.4 mJ·m^{-2}, with an only γ_s^p of 0.58 mJ·m^{-2} and a γ_s^d of 26.86 mJ·m^{-2}. The values of γ_s obtained were in agreement with the results previously reported for other authors [21].

APP promotes a remarkable increase in wettability of LDPE sheets. This is due to the action of several plasma-acting mechanisms: surface functionalization by insertion of polar groups and changes in surface topography [13,25,26].

The overall effects of APP can be observed in Figure 2, which shows the variation of γ_s, the polar γ_s^p and dispersive γ_s^d components of LDPE surfaces as a function of speed with a nozzle-surface distance of 6 and 10 mm.

(Figure 2)

From Figure 2, several conclusions can be obtained. Firstly, the tendency is highlighted in order to decrease the γ_s of the sample as the treatment rate is increased. It is observed a significant increase of the γ_s for low treatment rates (100, 200 and 300 mm·s^{-1}). For these processing conditions at low sample distance and low treatment rate, an increment can be obtained from 24 mJ·m^{-2} for the pristine sample, to values around 63 mJ·m^{-2}, for low treatment rate. This represents an increase around 130%. Moreover these results are in total agreement with previous studies of other authors, as Sanchis et al [27,28]. The second conclusion that can be extracted from Figure 2, is related to the influence of the distance between nozzle and surface sample of LDPE sheets. As the distance is increased, surface activation of the LDPE sheet is attenuated. Values of γ_S of the LDPE sheets treated of 10 mm are a 15% average lower than values obtained with a treatment of 6 mm. Therefore, the use of slow distances nozzle-surface of LDPE sheets and treatment rate is suitable to promote a more pronounced increase in surface wettability. Finally, as we can observe in Figure 2, the variation of the γ_S^p is the cause of the increase of the γ_S. With APP it is achieved a rise of 0.58 $mJ{\cdot}m^{-2}$ of a pristine sample to values above 41 $mJ{\cdot}m^{-2}$. The increase of the γ_S^d is representative for surface functionalization as a consequence of surface interlock of some polar groups (mainly oxygen based-moieties) [25]. Furthermore, the γ_S^d undergoes very little changes. There is only an average variation of 13% of γ_S^d between samples treated at slow or fast treatment rates in the two distances studied.

In general it is observed that the surface modification of LDPE sheets through the application of atmospheric plasma is due to insertion of polar groups and allows optimal functionalization of the polymer surface at low treatment rate and nozzle-surface distance [29,30].

On the other hand, additionally to surface functionalization, APP promotes some surface abrasion that leads to material removing and, subsequently topography changes [25].One of the main effects of treatment with APP is known as etching. This process consists in the formation of small craters and increased roughness of the treated surfaces due to the projected atoms and its energy. In polymeric materials, etching process also produces a rupture of covalent superficial bonds, which results in weight loss [31,32].

Etching and raised roughness in polymeric material act improving the wettability and adhesion properties [33].

Figure 3 shows the plot evolution of the weight loss and the increase of average roughness in terms of the two distances studied and the different treatments rate studied previously.

(Figure 3)

As it can be observed, the APP abrasion is much more aggressive and the weight loss reaches high values for low treatments rates for low sample distances. For a treatment rate of 100 $mm \cdot s^{-1}$ and 6 mm of sample distance, the APP aggressiveness is maximum, thus the high variation on weight loss in the sheet can be observed (0.0075% of mass total). When the treatment rate is increased, the aggressiveness of the plasma treatment is lower, and the sample weight loss is slight, as it is shown in the values for a treatment rate of 1000 $mm \cdot s^{-1}$ (0.0017%). In a distance sample distance of 10 mm, this value decreases 0.051 % in the most aggressive treatment conditions (100 $mm \cdot s^{-1}$) and 0.0011% for less aggressive treatment (1000 $mm \cdot s^{-1}$), which corroborates the attenuating effect of the sample distance.

The average roughness obtained with AFM technique has been compared with the roughness of a pristine sample. This pristine sample has an average roughness of 26.59 nm. The low surface roughness is one of the factors that negatively affects the wettability and subsequently adhesive processes [34]. The average roughness of the LDPE sheet treated with a 6 mm distance and 100 $mm \cdot s^{-1}$ value of treatment rate, is increased to 123.6 nm, representing a rise of 364.6%. For the same distance of treatment and 1000 $mm \cdot s^{-1}$ of treatment rate, the roughness is increased in 124%. On the other hand, with a distance of 10 mm, it is able to increase the average roughness in 202.8% for the most aggressive conditions (100 mm·s^{-1}), and in an 83.4% for maximum treatment rate.

By means of the Figure 3 it is demonstrated that the APP produces an increase of the surface roughness and a slight weight loss. The abrasion mechanism, related to material removing plays an important role. This fact could represent some restriction from an industrial point of view since abrasion is related together with substrate degradation. As the treatment rate and distance decrease, a remarkable increase in weight loss and average roughness is detected. This is due to the chain scission produced by the action of some species present in the plasma. Therefore if the APP technology is going to be introduced to an industrial process it must be taken into account the possible degradation. The aim is to optimize the best conditions of treatment rate and distance without coming to degrade the LDPE sheet. In this study, the minimum distance nozzle-surface of LDPE sheet is 6 mm and the minimum treatment rate is 100 mm·s^{-1}, because below conditions may be too aggressive for a LDPE sheets.

Prior to the study of the influence of the treatment rate and distance nozzle-surface in APP on the adhesive properties of shear test, the curing characteristics of the reactive polyurethane adhesive used to form the LDPE-LDPE sheets joints have been evaluated. The curing time of the adhesive is a key factor to determine the appropriate processing conditions in order to obtain the optimum mechanical performance of adhesive joints. With the aim of quantify this, the evolution of the maximum force registered in shear test in terms of the curing time (4, 10, 24 and 48 h) has been studied. The best adhesive performance (maximum force registered) has been achieved after 24 h. After this time, the maximum force remains practically constant. Therefore 24 h of curing time of the polyurethane is enough to ensure good adhesive properties.

(Figure 4)

Once the optimum curing conditions for the adhesive have been defined, the improvements on the adhesive properties of LDPE-LDPE sheets joints were evaluated. Figure 4 shows experimental results regarding changes in shear test in terms of sample distance of LDPE sheet and different treatment rates, 100, 300, 700 and 1000 mm·s^{-1}, with the aim of covering a wide range of the range of treatment rates. Previously, it should be taken into account that the maximum force registered of LDPE-LDPE joint without treatment is null. The results are in accordance with those described before regarding γ_S changes in terms of the distance and treatment rate. For a low treatment rate value, 100 mm·s^{-1}, the maximum force in shear test is increased to values above on a 200 N, in both distances studied. With higher treatment rates the maximum force decreases gradually. For example, with a treatment rate of 1000 mm·s^{-1} the maximum force is 27% and 30% lower than a rate of 100 mm·s^{-1} for 6 and 10 mm of sample distance respectively. With all conditions of treatment the maximum force registered in the shear test is much higher than a LDPE-LDPE joint without treatment, ensuring good mechanical joints that the industry demands for the use of polyolefin in sectors such as automotive, sports applications, toy industry, etc. In order to apply plasma treatments to industrial applications, it is necessary to know which requests are going to applied to the joint in order to choose the best treatment conditions.

All the results exposed above place plasma treatments as a mechanism able to improve the wettability and, consequently the adhesion properties in LDPE sheets for technological applications uses. It is important to remark that the main mechanism that leads to wettability improvement is surface functionalization by insertion of polar groups (oxygen-based species) together with a topography change (surface roughness and loss weight), but to a lesser extent. Moreover, one of the main advantages of the

APP is the simplicity of its operation and the possibility of operating continuously in an industrial process. Therefore it could be an ideal surface treatment technique for polyolefin materials. Nevertheless, it is well known that plasma treatments have an aging effect, namely, the plasma-treated polymers revert to their original surface properties gradually over time. By rotational and translational motions of chains and chains segments, the surface composition can change in order to minimize the interfacial free energy between the polymer surface and the environment [17]. The polar groups on the surface have the tendency to rotate or bury themselves from the surface to the bulk of the polymer [35]. Different authors have studied the influence of polymer crystallinity on the hydrophobic recovery [36] and also the influence of storage temperature [16], but up to now, limited numbers of papers have been published about aging effect of the APP in conditions simulating a common industrial process and the relation of this effect with adhesion processes. So the aim objective of this study is to choose the best treatment conditions (optimizing distance and treatment rate) and simulate the aging effect of the APP of the LDPE sheets that would occur in an industrial application. Subsequently the aging will be related with a shear adhesive process.

(Figure 5)

(Figure 6)

The ageing of the LDPE sheets treated with APP has been studied using contact angles measurements and the subsequent calculation of the γ_s. Figures 5 and 6 shows the evolution of the γ_s of the LDPE treated at 6 mm and 10 mm respectively, compared with pristine LDPE as a function of time of storage time. It has been evaluated the durability of the APP effects in terms of three treatment rates of treatment, 100, 300 and

700 mm·s^{-1} and the two studied sample distances. This assessment has been made to pristine material and material treated with plasma with aging times up to 21 days. For the first day a deeper analysis has been made, it has been taken measurements for 0, 3, 6, 9, 12, and 24 h after the specimens were subjected to the plasma treatment. It is observed that the ageing process for the two distances and the three treatment rates studied is characterized by a quick decrease in γ_S during the first hours of storage. The fact is that after three hours of treatment for a condition of 6 mm of distance and 100 mm·s^{-1} of treatment rate, the γ_S downs from 63 mJ·m^{-2} to 57 mJ·m^{-2}, representing a decrease of 10% respect a pristine sample. After 24 hours the decrease is 31% lower than the sample treated and analyzed immediately. That is, almost the third of the γ_S is lost in only 24 hours after the treatment. After 10 days, the γ_S is at 47% lower, which implies a speed of hydrophobic recovery much slower. Finally, after 21 days, the γ_S is almost similar to a sample without treatment.

The hydrophobic recovery is carried out mainly by the loss of polarity in the pristine surface of LDPE. As it can be observed, in any conditions of treatment studied, the γ_S^p decreases more abruptly than the γ_S^d. For example, in a pristine sample the γ_S^p is the 2% of the total contribution. If the sample of LDPE is treated in the most aggressive conditions (6 mm and 100 mm·s^{-1} of treatment rate), the γ_S^p ascend to contribute a 65% of the γ_S. The γ_S^p decreases 13.6% only in three hours of ageing time. After 1, 10 and 21 days the lost is a 15, 24 and 78% respectively. In contrast the γ_S^d only varies by 12% between the sample analyzed immediately after the treatment and a sample treated and ageing for 21 days.

The same trend has been observed in Figure 6, for a treatment with 10 mm of distance and a treatment rate of 100 mm·s^{-1}, which are aggressive conditions. In such conditions, after three hours of ageing period the γ_S has decreased 16%. This trend continues and after 1, 10 and 21 days, the γ_S falls 41%, 50% and 60 % respectively. This drop is caused by the loss of polarity, as it is shown in the fall of the γ_S^p a 87.3% respect a pristine sample and a sample treated and aged for 21 days. Under less aggressive conditions, with higher rate and sample distance (10 mm and 700 $mm\cdot s^{-1}$), the sample denominated 0 hours of ageing has been analyzed immediately after the treatment with plasma air pressure. It presents much less wettability, as result of the lower graft of polar molecules (C=O, -COOH, -C-O-C, etc.) in the surface of LDPE sheet. Hydrophobic recovery rate is slower due to the lower density of γ_S^p in the surface of LDPE sheet, since the γ_S is almost similar respect a sample analyzed immediately after 24 hours. Despite this, after 21 days of ageing time the sample of LDPE has the same wettability as a pristine sample.

This effect is mainly due to the reorientation of induced polar chemical groups into the bulk of the material, as Morent et al. explained [37]. Moreover the ageing in a non-polar environment force to the polar groups to recombinate or to react with functional groups of the environment. Both the rearrangement of oxygen-containing moieties such as the reorientation of polar groups from surface to bulk lead hydrophylicity to decrease [21]. Therefore, through the study of ageing it has been demonstrated that the graft of chemical moieties of polar nature (carboxyl, carbonyl, hydroxyl, amide, etc.) due to the plasma flux impact is not permanent. This characteristic has already been studied by some authors [38,39]. In addition, authors have studied a similar plasma system which obtains extreme durability in LDPE sheets (up to 270 days). This extreme effect is due to the work in very aggressive conditions with a sample distance of 6 mm and a treatment rate of 16 $mm\cdot s^{-1}$. Our opinion is that a treatment at such a low treatment rate could produce an extreme abrasion and a possible degradation and oxidation of the LDPE sheet.

The loss of polarity affects the storage times in industrial processes, where good adhesion properties are required. As it has been demonstrated, the samples treated and stored for 21 days, behave like a pristine sample, resulting in poor wettability properties.

Following with the optimization of the best treatment conditions, it has been demonstrated that at slow treatment rates (100 $mm \cdot s^{-1}$) and short sample distances (6 and 10 mm), the best surface modification are achieved. Once the optimum conditions of work for the modification of LDPE sheets have been defined, we have proceeded to study the effect of the ageing on adhesion shear processes. So finally, the influence of ageing will be shown with the maximum force obtained in shear test of LDPE sheets treated with these two conditions since they are the optimum to be applied in an industrial process.

(Figure 7)

Figure 6 shows experimental results regarding changes in shear essays in terms of treatment conditions and storage time for the aging. It can be seen clearly, a decrease of the maximum force in the shear test as a consequence of the ageing process. It is appreciated a similar behavior independently of the sample distance. After 1 day of storage time, the maximum force has been reduced by 25% for both working conditions respect a sample treated and joined immediately. After 21 days the maximum force is 64% lower for both treatment conditions, which shows the relationship between wettability and adhesion properties. In spite of the values of γ_S after 21 days they are similar to a pristine sample; the adhesive properties are much higher due to the physical changes carried out in the polymer surface (increase of roughness and loss of weight) and the greater presence of polar molecules.

4. CONCLUSIONS

In this paper, an optimization of the treatment conditions of APP treatment on LDPE sheets has been carried out, and also the aging effect on the treated sheets has been quantified. APP treatment is an appropriate surface modification procedure of LDPE sheets in a continuous way. Among the different variables to be considered as key factors for the process, the treatment rate has resulted to be the most relevant. We have confirmed that APP treatment considerably activates the surface of LDPE sheets by means of γ_s enhancement.

A treatment rate of 100 mm·s^{-1} is enough to provide good surface wettability (the γ_s is increased from 27 mJ·m^{-2} up to values of 64 mJ·m^{-2}). A decreasing tendency of the solid γ_s can be observed as the treatment rate increases, reaching down to 50% with a treatment rate of 1000 mm·s^{-1}. This fact can be attributed to the insertion of chemical moieties of polar nature due to the plasma flux impact, this is shown by the increment of γ_s^p, which increases from 0.58 mJ·m^{-2} up to 40 mJ·m^{-2}. The etching effect caused by the impact of the air flux onto the polymeric surface has been analyzed using both AFM technique and also measuring the weight loss. These studies revealed the increment of surface roughness and a slight weight loss.

This chemical and morphological change in LDPE sheets ensures good adhesive properties. Working in optimal conditions, it is possible to increase the maximum force in shear test to over 200 N while that the initial shear force is null (without APP treatment).

The ageing caused by the reorientation of polar groups from the surface into the bulk of the material, causes a loss of wettability and adhesive properties, up to 60% after 21 days of ageing. It should be taken into account that the most hydrophobic recovery occurs in the first moments after the treatment, as it shows a decrease of 25% after 24 hours of the treatment. The combined effect of moderate temperature (25ºC) and relative humidity (30%) influences in this rate loss in the maximum force in shear test. Therefore it can be concluded that working in optimal conditions (low threating rate and sample distance) increments substantially the adhesive properties, as well as the results stability which enables the application of the technique in an industrial environment.

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Figure Caption:

Figure 1. Scheme of APP device.

Figure 2. Variation of surface energy and polar and dispersive components as a function of treatment rate for a different samples distance: a) 6 mm, b) 10 mm.

Figure 3. Variation of average roughness and weight loss as a function of treatment rate and sample distance: a) 6 mm, b) 10 mm.

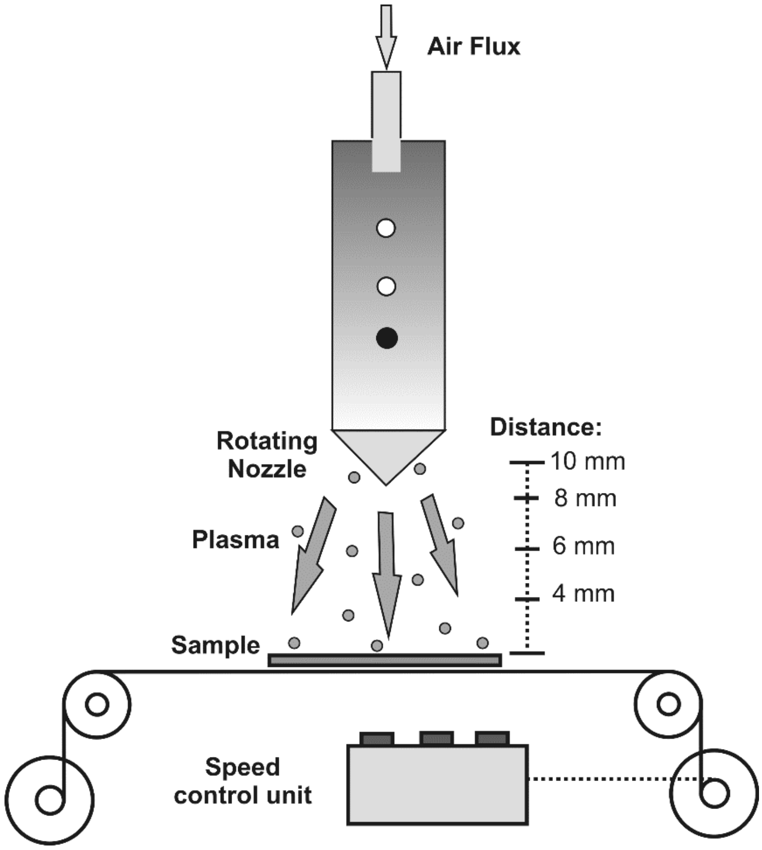
Figure 4. Maximum force in shear test as a function of treatment rate and sample distance: a) 6 mm, b) 10 mm.

Figure 5. Evolution of the γ_S as a function of aging time of samples treated with distance of 6 mm for different treatment rate: a) 100 $mm \cdot s^{-1}$, b) 300 $mm \cdot s^{-1}$, c) 700 $mm \cdot s^{-1}$.

Figure 6. Evolution of the γ_S as a function of aging time of samples treated with distance of 10 mm for different treatment rate: a) 100 $mm \cdot s^{-1}$, b) 300 $mm \cdot s^{-1}$, c) 700 $mm \cdot s^{-1}$.

Figure 7. Maximum force in shear test as a function of aging time and 100 $mm \cdot s^{-1}$·treatment rate and different sample distance: a) 6 mm, b) 10 mm.

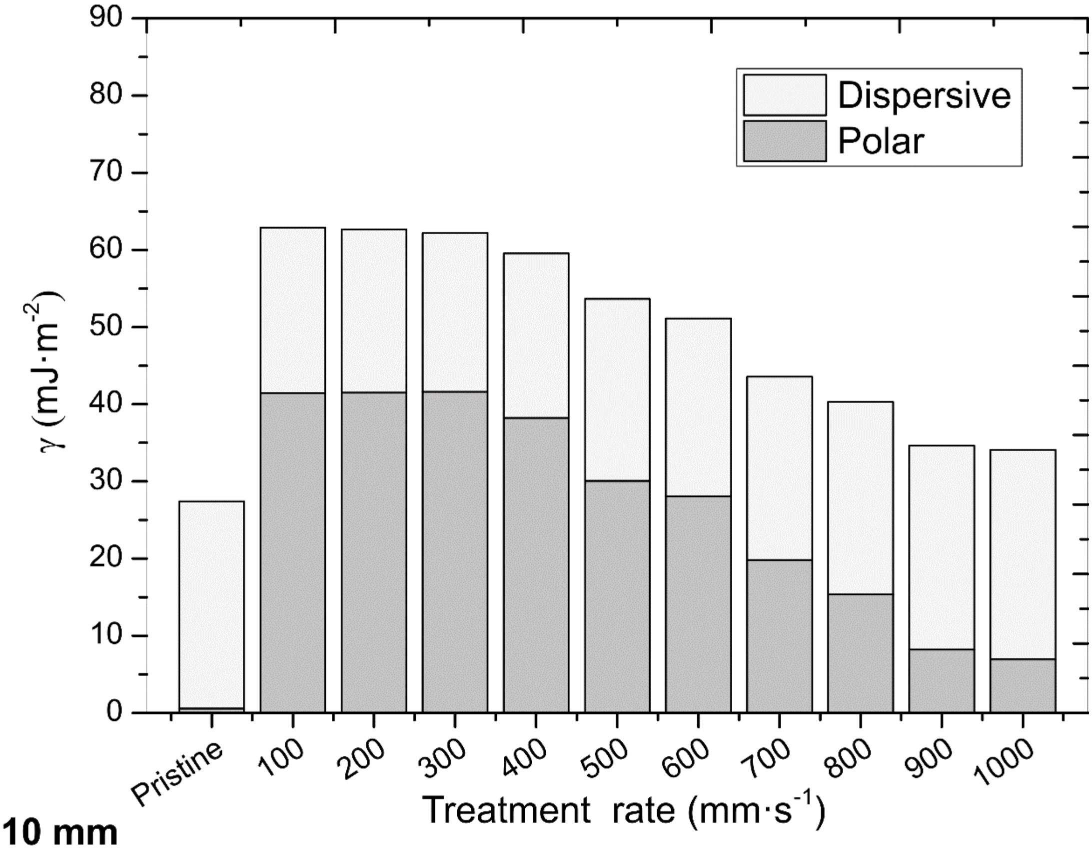
Figure 1.



Air Flux
Rotating
Nozzle
Distance:
10 mm
8 mm
6 mm
4 mm
Plasma
Sample
Speed
control unit

Figure 2.

a) 6 mm



b) 10 mm

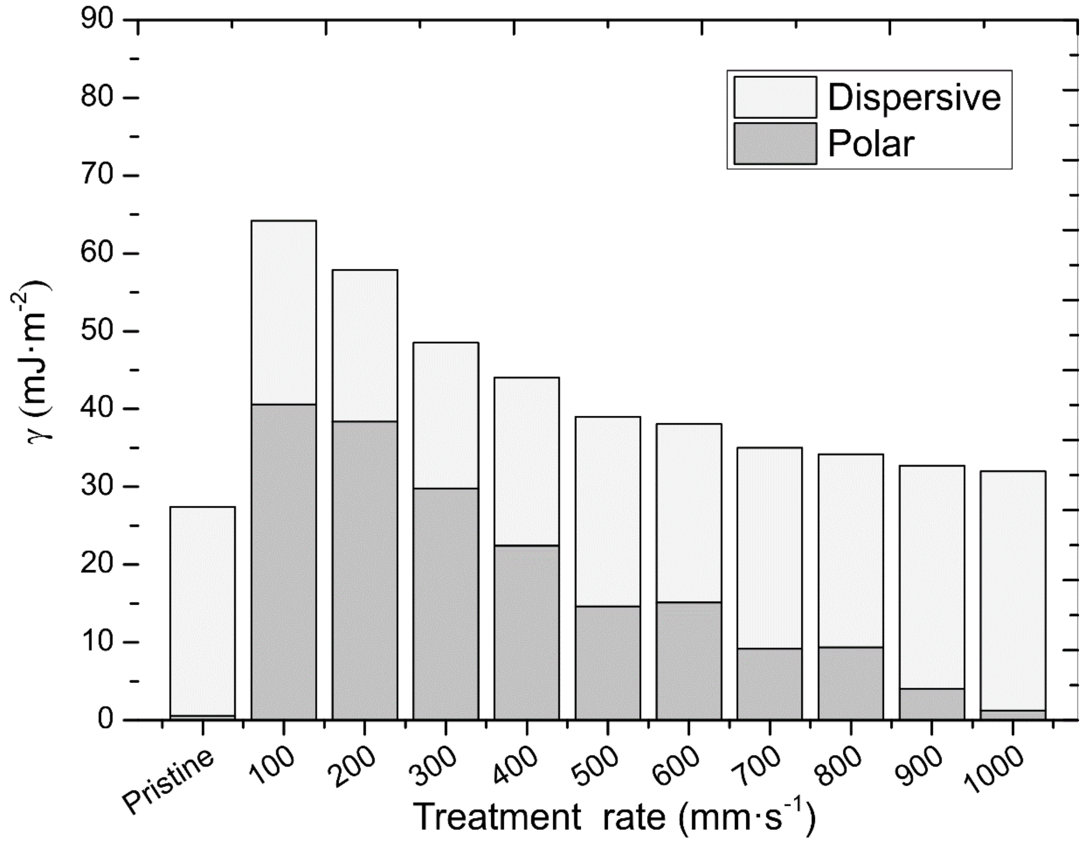
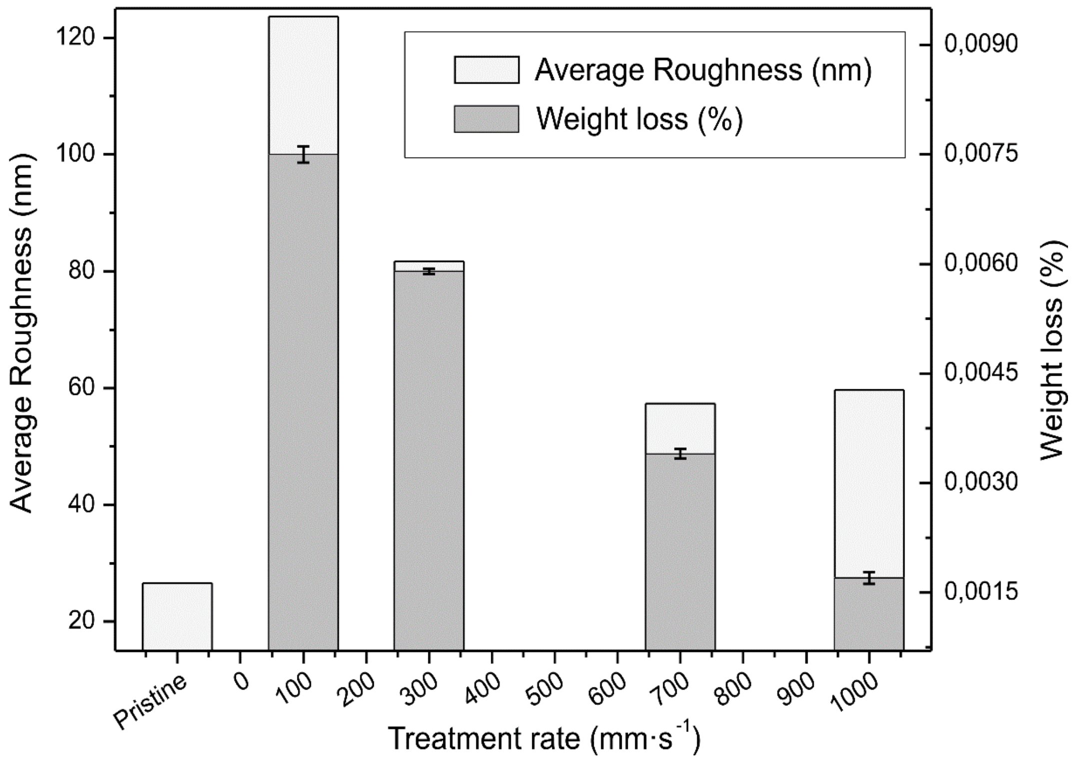


Figure 3

a) 6 mm



b) 10 mm

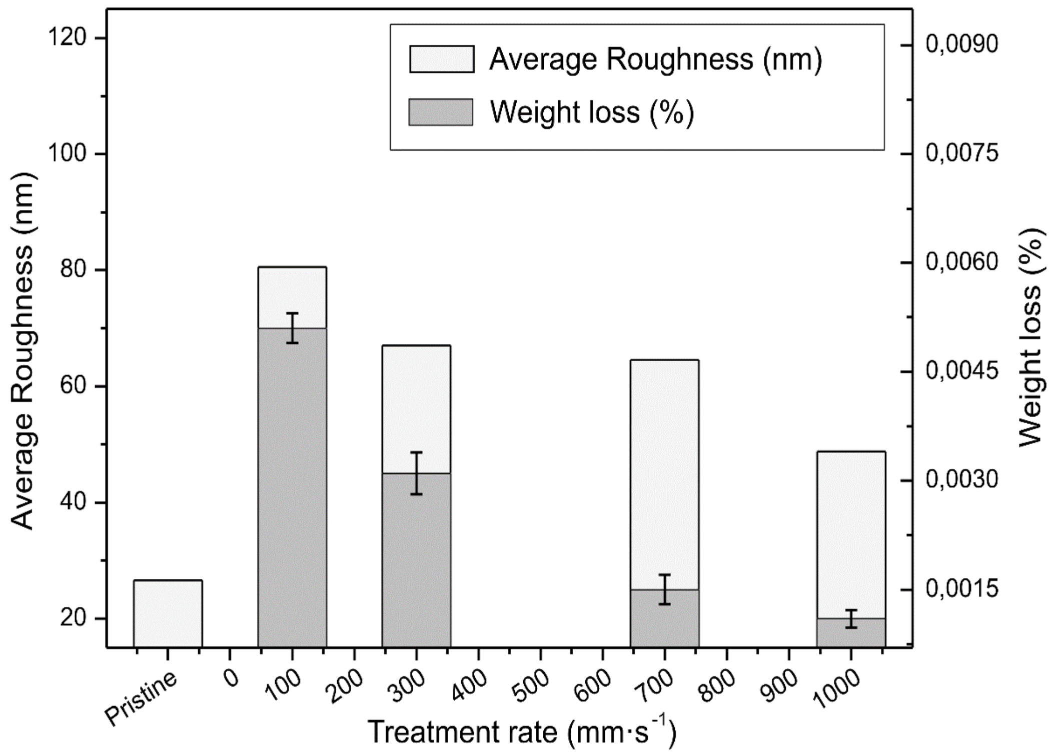
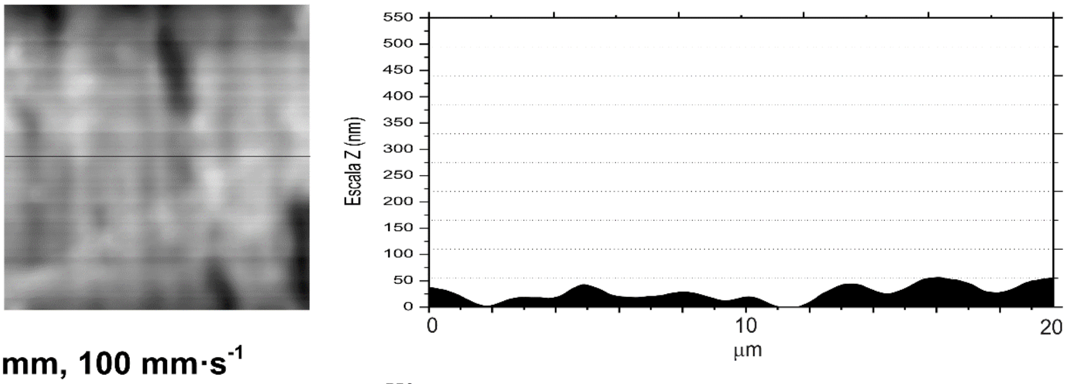


Figure 4.

a) pristine sample



b) 6 mm, 100 mm·s^{-1}

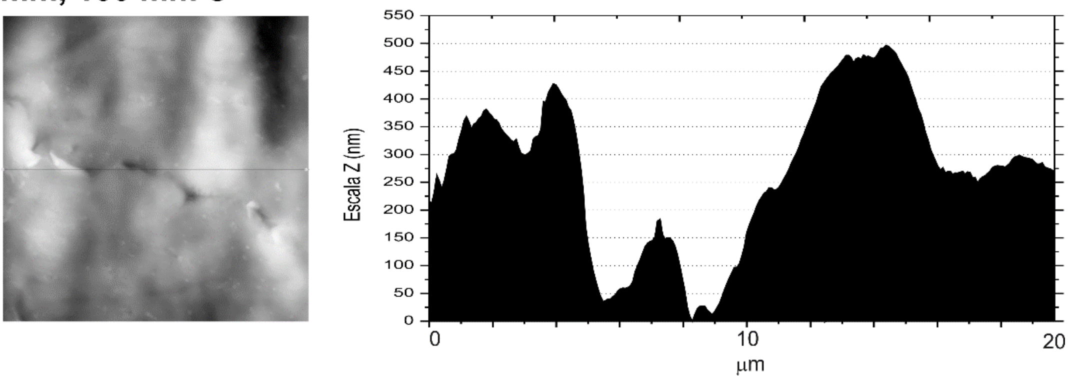
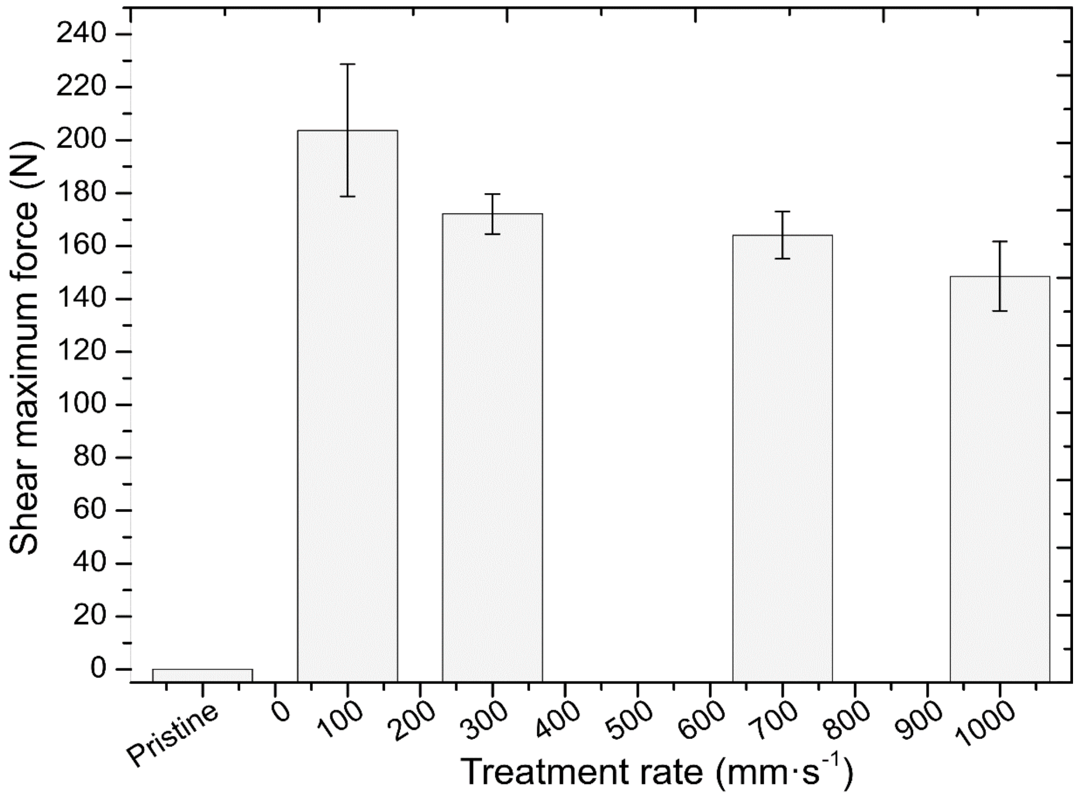


Figure 5

a) 6 mm



b) 10 mm

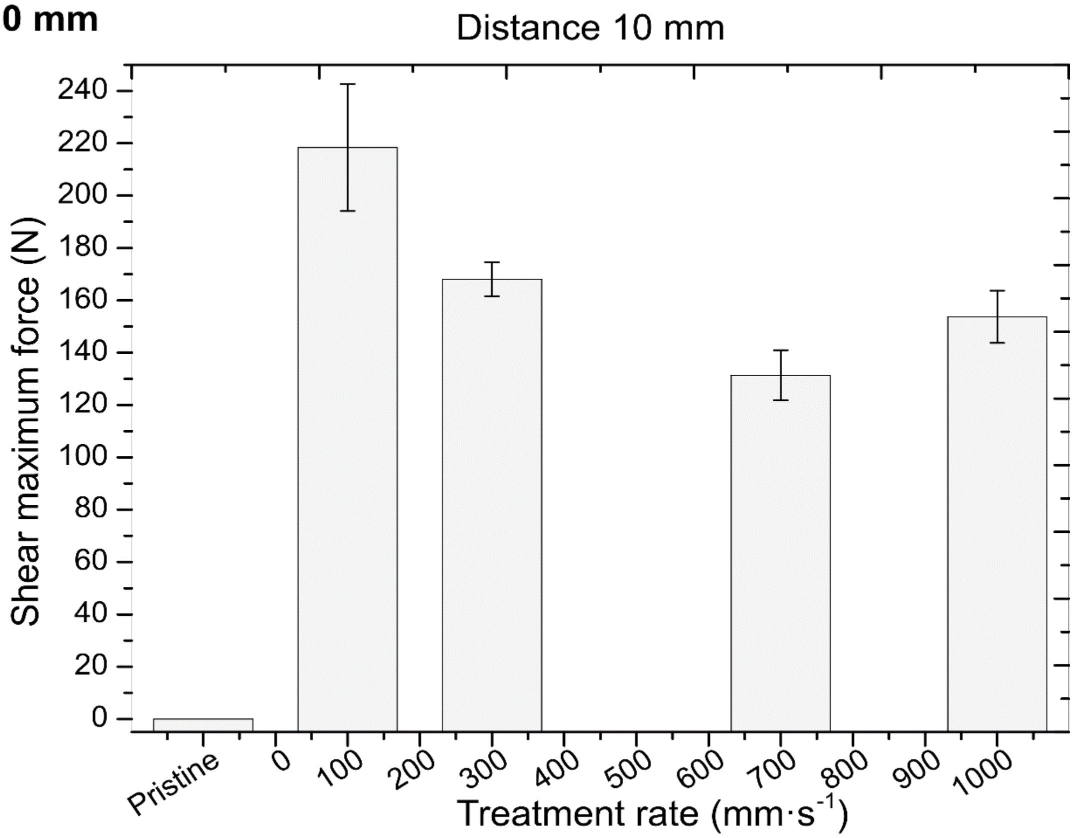
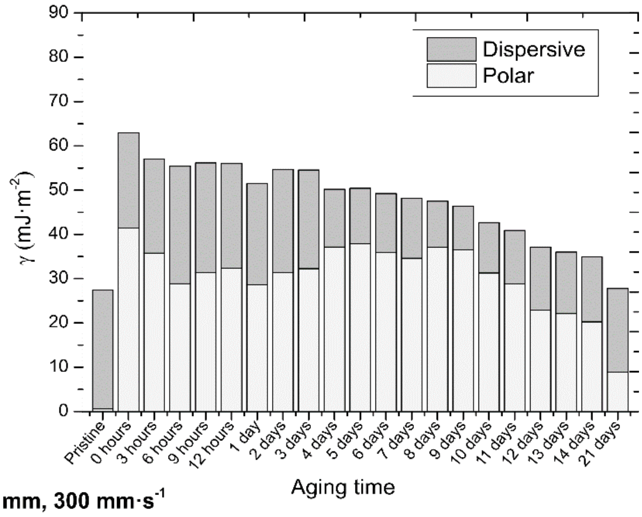
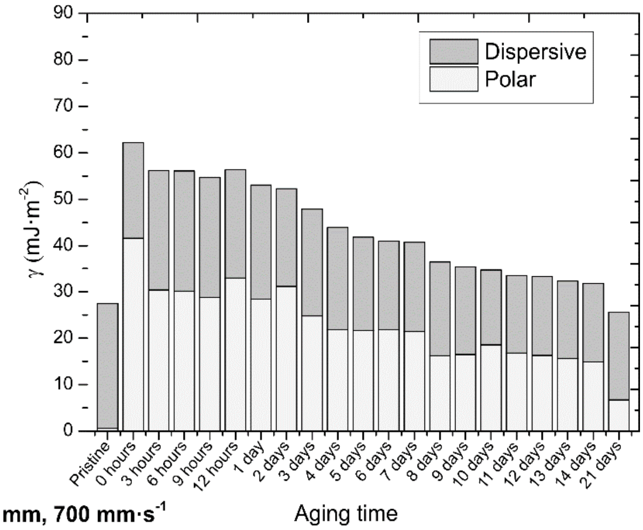


Figure 6

a) 6 mm, 100 mm·s^{-1}



b) 6 mm, 300 mm·s^{-1}



c) 6 mm, 700 mm·s^{-1}

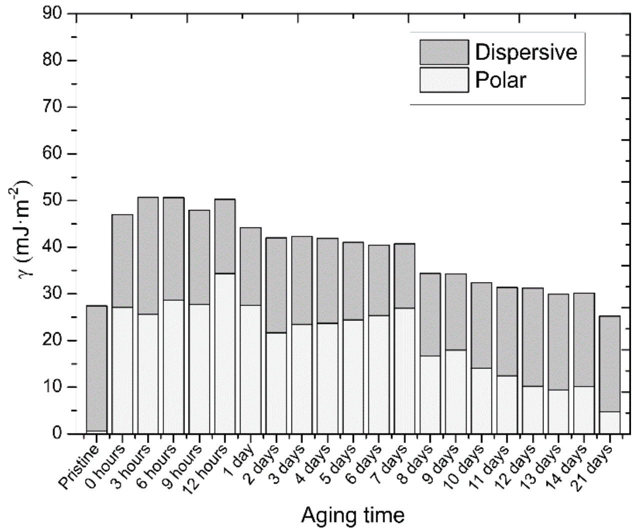


Figure 7.

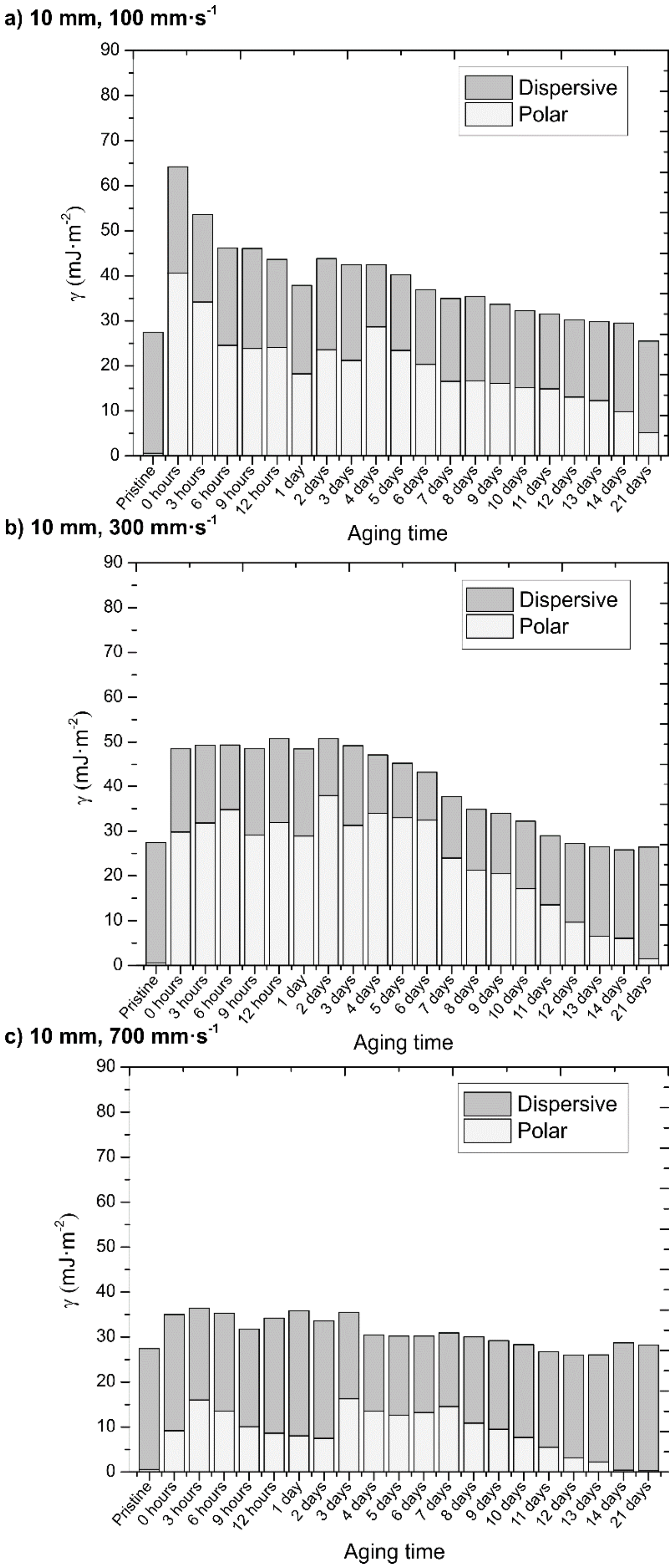
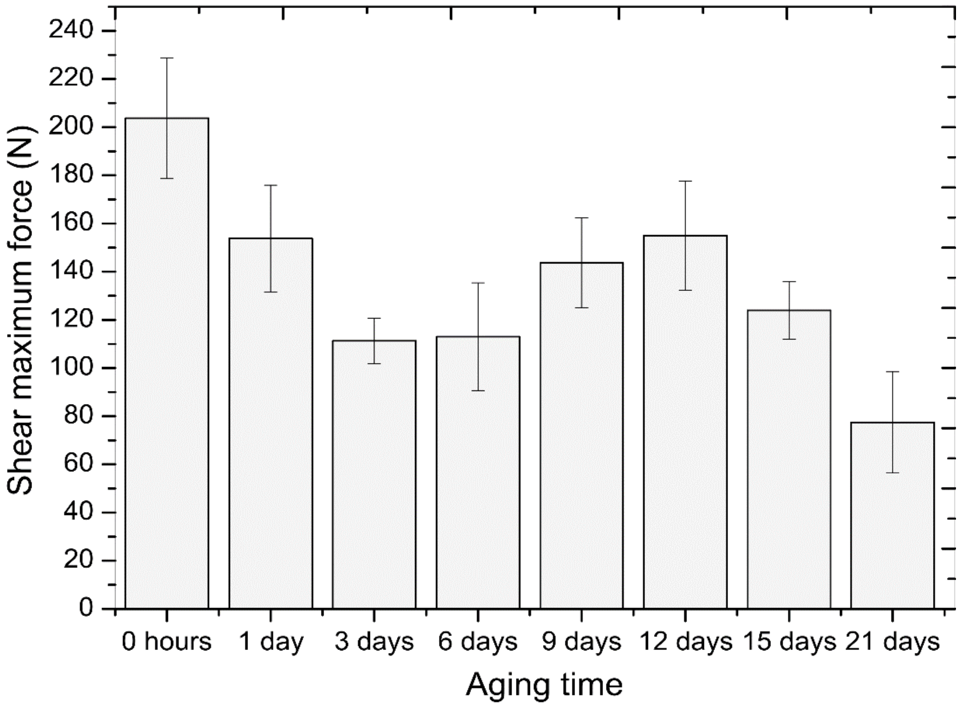

a) 10 mm, 100 mm·s-1
b) 10 mm, 300 mm·s-1
c) 10 mm, 700 mm·s-1
Dispersive
Polar
γ (mJ·m-2)
Aging time
Pristine
0 hours
3 hours
6 hours
9 hours
12 hours
1 day
2 days
3 days
4 days
5 days
6 days
7 days
8 days
9 days
10 days
11 days
12 days
13 days
14 days
21 days
0
10
20
30
40
50
60
70
80
90

Figure 8.

a) 6 mm, 100 mm·s⁻¹



a) 10 mm, 100 mm·s⁻¹