Hydrophobic recovery of low density polyethylene treated with corona discharge plasma

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INTRODUCTION

The uses in textile laminates of low density polyethylene (LDPE) like a film form, need an important optimization on their adhesion surface properties, because these polymeric films offer very low surface energy values (lower than 30 mJ·m^{-2}). So, in order to obtain laminates, these polymer films need some surface treatments (chemical, thermal, electrical). One of the most interesting industrial treatments, that permits increasing adhesive properties on the polymeric film by improving its surface energy, is corona discharge plasma treatment. The polymeric films treated with corona discharge plasma show a remarkable increase in wettability properties as a consequence of the surface activation, thus increasing surface energy values (γs) and promoting a hydrophilic character One of the most interesting treatments is that based on plasma technology because it is an environmental friendly technology and promotes high surface energy values and, consequently, improve adhesive properties [1-10]. In this work, we have used corona discharge plasma technology to modify wettability properties of a low density polyethylene and make it useful for laminates with other films or foams. We have evaluated the influence of the working power and a complete study of the plasma-acting mechanisms has been carried out. Furthermore, since these laminates are to be used in technological applications, we have studied the influence of the temperature and relative humidity on the mechanical properties of the adhesion joints [11-17].

EXPERIMENTAL

The film used for the study was a low density polyethylene (LDPE) with improved flexibility due to the presence of EVA, and ethylene-vinyl acetate copolymer, with a thickness of 50 µm and a density of 0.92 g.cm^{3}.

Low density polyethylene films were exposed to a continuous corona discharge plasma treatment, with constant film flow of 15 m/min. The distance between electrodes was fixed at 1.5 mm. The corona discharge generator operates at 50 Hz with a maximum power of 1kW. This equipment was supplied by FABRILEC S.L., mod. GF-100-BADIA (Fabrilec, S.L., Valencia, Spain).

Surface wettability changes have been evaluated using contact angle measurements with different test liquids for calculate surface energy. Static contact angle measurements were carried out at room temperature on a KSV CAM 200 goniometer

(KSV Instruments, Helsinki, Finland) using water, glycerol, diiodomethane and formamide as test liquids with different polarities. The maximum error in the contact angle average values did not exceed ± 3%. The initial contact angles measurement was made 5 minutes after the plasma treatment. The Owens-Wendt method was chosen to calculate surfaces energies because it takes dispersive and polar components into account.

Characterization of the surface changes due to the plasma functionalization mechanism has been carried out using X-ray photoelectron spectroscopy XPS with a VG-Microtech Multilab electron spectrometer (VG Mictotech Ltd, Uckfield, UK), using the Mg Kα radiation (1253.6 eV) from a twin anode working in constant energy mode at a pass energy of 50 eV.

RESULTS AND DISCUSSION

- Influence of working power of the plasma corona treatment

An important increase in surface wettability has been observed with the working power in the plasma treatment. The initial surface energy (γ_s) value (27.6 mJ.m^{-2}) increases rapidly to maxim value for 600 W (45.5 mJ.m^{-2}). For greater working powers, the surface energy is lower due the degradation stage of the treated surface for the aggressively of plasma treatment conditions. The same effect is observed on the polar (γ_s^p) and dispersive (γ_s^d) components of surface energy. This increase in surface hidrophility is due to introduction of functional polar groups on polymer surface treatment. (figure 1)

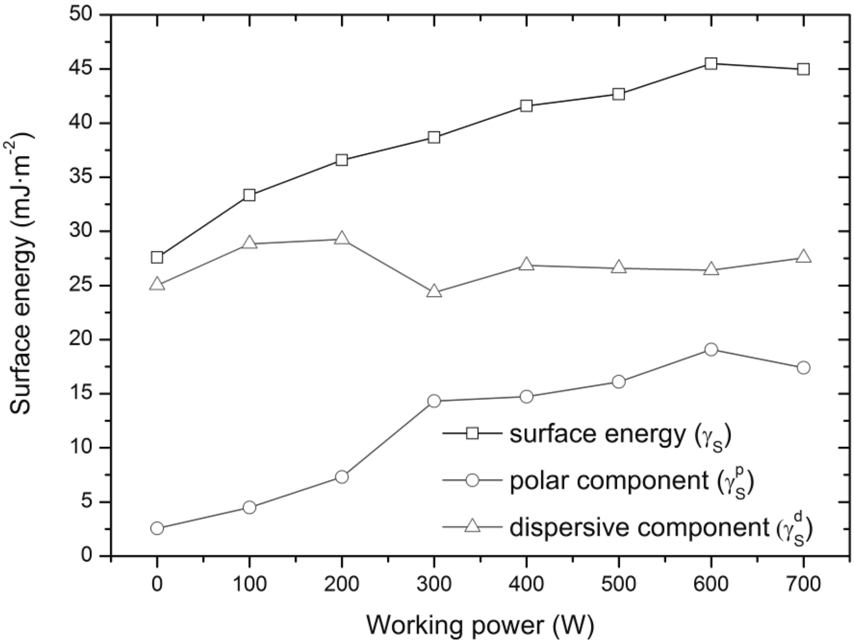

Figure 1.- Variation of surface energy (γ_S), polar (γ_S^p) and dispersive (γ_S^d) components on the low density polyethylene with the increase of working power.

The different species in the atmosphere of plasma corona treatment promote the formation of great amount of instable species and free radicals, the action of an oxidizing atmosphere (air) promotes certain reactions with oxygen and water that enhance surface activation as XPS low resolution scans reveal (table1 and 2). The contribution of the O 1s increases with treatment working power while contribution of N 1s remains almost constant. The C 1s peak can be resolved into three contributions related with oxygen-based species. In this sense, one can note that the surface functionalization process induced by corona discharge plasma treatment is based on the insertion of different oxygen containing species like hydroxyl, peroxide, hydroperoxide, ether, ester, carbonyl and carboxyl groups.

Table 1.- Composition of LDPE film surface (% atomic) obtained with XPS analysis like a function of working power in corona discharge plasma treatment.

Working power (W)	**% C atomic**	**% O atomic**	**% N atomic**	**ratio O/C**	**ratio N/C**
0	93,3	4,0	2,7	0,04	0,03
200	88,2	8,9	2,9	0,10	0,03
400	86,5	10,7	2,7	0,12	0,03
600	86,7	10,3	2,9	0,12	0,03

Table 2.- Relatives contributions of the different C presents in the C 1s peak deconvolution like a function of working power in corona discharge plasma treatment.

Working power (W)	**% $C_{(I)}$ [–C–C–], [–CH_2–]**	**% $C_{(II)}$ [–C–O]**	**% $C_{(III)}$ [–C=O]**
0	93,1	6,2	0,7
200	87,0	9,4	3,6
400	84,5	11,3	4,2
600	86,6	10,2	3,2

The corona discharge ionizes species present in the air, and these highly unstable species interact with the polymeric chains closest to the surface, leading to polymer chains scission and the consequent formation of free radicals. These free radicals act as points of insertion for polar species which contribute positively to increases in the surface energy of low density polyethylene film [15-17].

- Plasma Corona treatment durability

Figure 3 shows comparatively, the evolution of the total surface free energy (γ_S) of LDPE film treated with corona discharge plasma in terms of the aging time using three storage conditions: air at room temperature; at controlled conditions T=23ºC; R.H.=50%; and T= 50ºC; R.H.=40%. In the three cases, we can observe a remarkable decrease in surface free energy (γ_S) for short aging times. After the first day of the different aging cycles, we can see that the surface energy is reduced in a small (1.2-3.5 %) way for non-aggressive conditions (air at room temperature, T=23ºC; R.H.=50% respectively) but in the case of thermal aggressive aging conditions, the surface free energy is reduced in a remarkable way up to values close to 11 %. This high decrease promoted by thermal aggressive conditions is due to the negative effect of temperature on wetting durability; temperature promotes diffusion processes that control the re-arrangement mechanism of polar groups and migration of LMWOM from the plasma-treated polymer surface towards the bulk material. The use of aggressive thermal aging conditions cause the acceleration of the aging process as it can be observed in Figure 3.

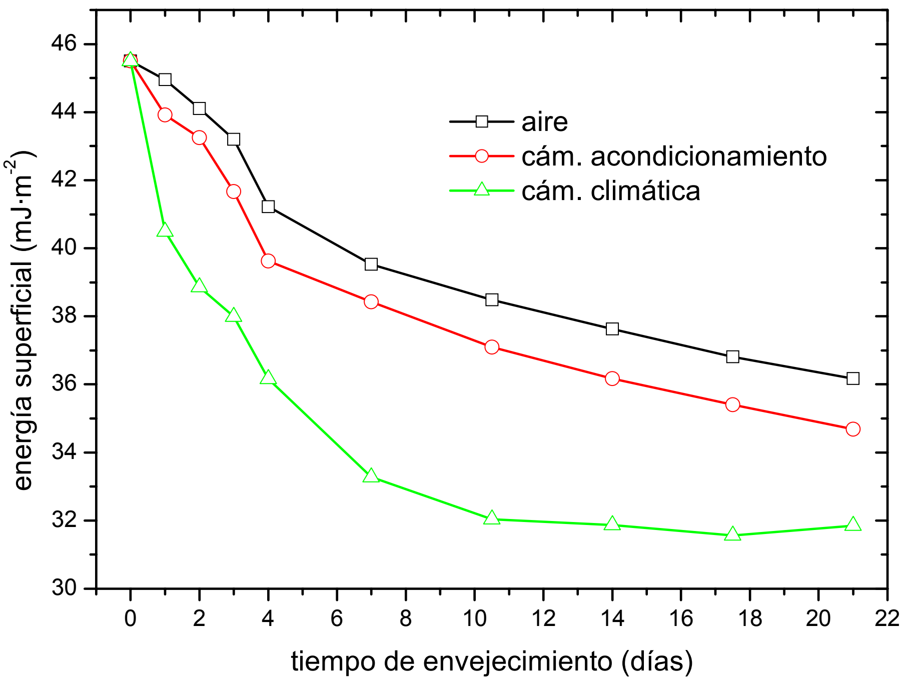

Figure 3.- Variation of the total surface energy (γ_S) of LDPE film treated with corona discharge plasma (P=600 W) in terms of the storage time for different aging conditions.

CONCLUSIONS

The results show that working powers in the 600 W range are the most appropriate for low density polyethylene. By using these working powers it is possible to increase wettability in a considerable way and, consequently, improving adhesion properties. The study of the plasma-acting mechanisms show that functionalization is one the main mechanisms together with some roughness changes. But is observed an important tend to aging on corona-treated film polymeric surface, this phenomenon is called hydrophobic recovery. This must be taken into account when using plasma-treated films for laminates' preparation, since adhesion properties are rapidly lost as a consequence of the aging process. These treated films show average durability in terms of the storage conditions (temperature-humidity) thus it is possible to obtain laminates for technical applications using corona discharge plasma technology.

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