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María Dolores Landete-Ruiz, José Miguel
Martín-Martínez

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IMPROVEMENT OF ADHESION AND PAINT ABILITY OF EVA COPOLYMERS WITH DIFFERENT VINYL ACETATE CONTENT BY TREATMENT WITH UV-OZONE

María Dolores Landete-Ruiz, José Miguel Martín-Martínez*

*Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante,
Spain.*

* To whom all correspondence should be addressed. Phone: +34-96-5903977.
Fax: +34-96-5909416. E-mail: jm.martin@ua.es

Abstract

The surface modifications produced by UV-ozone treatment of two ethylene-vinyl acetate (EVA) copolymers containing 12 and 20wt% vinyl acetate (EVA12 and EVA20 respectively) were studied. The treatment with UV-ozone improved the wettability of both EVAs due to the creation of new carbon-oxygen moieties on their surfaces. The extent of these modifications increased with increasing the length of the treatment and the modifications produced in EVA20 were produced for shorter lengths of treatment. The UV-ozone treatment also created roughness and heterogeneities on the EVA surfaces. Whereas roughness formation prevailed on the UV-ozone treated EVA12, important ablation was dominant on the treated EVA20. T-peel strength values in joints made with polychloroprene adhesive increased when the EVAs were treated with UV-ozone. Short length of UV-ozone treatment (1 min) produced higher T-peel strength in joints made with EVA20 whereas higher T-peel strength values in joints made with EVA12 were obtained after treatment for 5-7.5 min in which a cohesive failure into a weak boundary layer on the treated EVA surface was found. Furthermore, the adhesion of UV-ozone treated EVA20 to acrylic paint increased. Finally, the ageing resistance of the treated EVA/polychloroprene adhesive joints was good and the surface modifications on the UV-ozone treated EVAs lasted for 24 hours after treatment at least.

Keywords: B. Polyolefins; B. Surface treatment; C. Peel.

1. INTRODUCTION

Ethylene vinyl acetate (EVA) copolymers have been widely used in recent years as midsole and insole materials in the footwear industry. Due to their excellent mechanical properties, low hardness and flexibility, those elastomeric polyolefins are used in the toy and childcare industry too. However, adhesion of EVA copolymers to adhesives and paint is poor due to their low surface energy. Adhesion of EVA copolymers has been improved by means of adhesion promoters before adhesive application. Corona discharge and low-pressure plasmas have been also studied as effective surface treatments of EVA leading to oxidization on the surface, increasing its surface energy and creating surface roughness [1-4].

Traditionally, surface treatment with UV-ozone has been used for removing organic contaminants on different polymer surfaces [5]. The photons produced by UV-ozone irradiation have sufficient energy to break most of the C-C bonds and also induce chain scission and cross-linking on polymer surfaces [6-9]. More recently, UV-ozone has been developed as an alternative surface treatment for increasing the wettability of poly(ethylene terephthalate) (PET), polyethylene (PE), polypropylene (PP) and different rubbers [6,10-13]. Furthermore, improved wettability and high peel strength values after treatment with UV radiation were demonstrated for different rubbers, and the extent of the surface modifications increased by increasing the length of treatment [13,14].

Previous study [15] has shown that the UV treatment of EVA containing 12wt% vinyl acetate (EVA12) improved its wettability and polar moieties were produced on the surface, leading to an increase in adhesion. Properties such as crystallinity, melting point, flexibility, and glass transition (T_g) among others [16] are influenced by the vinyl acetate content (VA) of EVA copolymers and the adhesion properties of EVA are also affected by their VA content [17,18].

A systematic study dealing with the comparative surface modifications, adhesion and durability of UV-ozone treated EVA copolymers with different VA content have not been carried out yet. Therefore, in this study the surface modifications and their stability produced by treatment with UV-ozone of two EVA copolymers with different VA content (EVA12 and EVA20) were compared, and the effect on their adhesion properties to polychloroprene adhesive was evaluated. In addition, the paint ability of the EVA surfaces was studied.

2. EXPERIMENTAL

2.1. Materials

EVA copolymers with different VA content were supplied by Repsol Química, S.A. (Santander, Spain). The main properties of the EVA copolymers are summarized in Table 1 [19]. These copolymers were received as pellets and moulded using a Margarit JSW injection machine (Barcelona, Spain) to obtain test samples of 150 x 60 x 2 mm³. Moulding conditions of the EVAs were as follows : Injection temperature : 200 °C; injection time : 6 seconds; backward pressure : 60 % of total pressure (1570 bar; 1bar = 105 Pa); injection flow : 70 % of total flow (113 cm³/s) ; cooling time : 22 seconds; and temperature of the mould : 20 °C. Moulded EVA samples were cut into 150 x 30 x 2 mm³ pieces for adhesion tests. Two identical treated EVA samples were used to produce adhesive joints.

Adhesive joints of UV-ozone treated EVAs were made using a two-component solvent born commercial polychloroprene adhesive (Telcopren 3003) - supplied by Composan Adhesivos S.A. (San Vicente del Raspeig, Alicante, Spain) - containing 5 wt% polyisocyanate (Desmodur RFE) - supplied by Bayer AG (Leverkusen, Germany). Polyisocyanate was added as a crosslinking agent just before adhesive application.

Acrylic paint supplied by Ferber S.A (Granollers, Barcelona, Spain) and adhesive rubber tape 3997 (3M ESPAÑA, Madrid, Spain) were used to prepare tape/paint/EVA joints intended for adhesion tests.

2.2. Experimental techniques.

2.2.1. UV-ozone treatment. The UV-ozone treatment was carried out by using a low-pressure vapour grid mercury lamp manufactured by American Ultraviolet (USA). This lamp operates at the wavelength of 254 nm (major) and 195 nm (minor) and provides a power of 10 mW/cm² measured at a distance of 2.54 cm from the EVA surface. The UV lamp was placed inside a box made of UV-resistant polycarbonate; an exhaust fan was used to avoid both the local concentration of ozone during treatment and the over-heating of the lamp. The distance between the UV source and the EVA sample was set to 2 cm. The length of the treatment was varied between 1 and 7.5 minutes.

2.2.2. Contact angle measurements. Contact angle measurements were carried out in a thermostated chamber (25 °C) using a Ramé Hart 100 goniometer (Netcong, NJ, USA). The chamber was previously saturated with the vapor of the test liquid at 25 °C (bidistilled and deionized water) for at least

10 minutes before the measurement. Drops (4 μl) of test liquids were placed on the EVA surface using a micrometric syringe. Advancing contact angles (tilting plate method) were measured immediately after UV treatment. Five replicas were measured at least until an experimental error of $\pm 2^\circ$ was obtained.

2.2.3. ATR-IR spectroscopy. The ATR-IR spectra of the EVA surfaces before and after UV treatment were obtained to evaluate the chemical changes produced within a surface thickness of about 5 μm [20]. The attenuated total multiple reflection technique was employed (ATR-IR). A Nicolet FTIR 5DXB spectrometer (Agilent Technologies, Murcia, Spain) provided with a thallium bromo-iodide prism (KRS-5) was used. The incident angle of the IR radiation was 45° . Two hundred scans were obtained and averaged at a resolution of 4 cm^{-1} .

2.2.4. X-ray photoelectron spectroscopy (XPS). A VG Scientific Microtech Multilab spectrometer with $\text{MgK}\alpha$ X-ray source (1253.6 eV) operating at 15 keV and 300 W and using a pass energy of 50 eV was used. The pressure inside the analysis chamber was held below 5×10^{-8} Torr during the course of the analysis. Square sample pieces (5 mm x 5 mm) were used and cooled using liquid nitrogen. The measurements were made at a take-off angle of 45° . Survey scans were taken in the range 0-1200 eV and narrow scans (20 eV) were obtained in significant peaks in the XPS survey spectra. Binding energies were referenced to the C1s at 285.0 eV. Multicomponent C1s photopeaks were curve fitted using a 30 % Gaussian/Lorentzian function with a full width at half-maximum (FWHM) of 1.80 eV.

2.2.5. Scanning electron microscopy (SEM). A JEOL JSM-840 microscope was employed to analyze the topographical modifications on the EVAs treated with UV-ozone. Samples were gold coated before analysis. The energy of the electron beam was 20 kV.

2.2.5. Atomic force microscopy (AFM). A NanotecTM microscope (Madrid, Spain) operating in tapping mode was employed to analyze the roughness on the UV-treated EVAs. Tapping mode was used to avoid irreversible damage on the soft EVA surfaces [21]. The cantilever deflection was monitored by a laser

beam. SiN₃ pyramidal cantilevers from Olympus ($k \cong 0.75$ nN/nm) were used. The cantilever operated at a frequency of 22 kHz. AFM micrographs were obtained using WSxM image analysis software (NanotecTM).

2.2.6. T-peel strength. Adhesive joints using two similarly treated EVA samples (150 x 30 x 2 mm³) were produced. The polychloroprene + 5 wt% polyisocyanate adhesive solution was applied with a brush on the EVA surface and the solvent was allowed to evaporate at room temperature for 30 min. The dried solid adhesive films on the EVA surfaces (about 50µm) were then melted at 75°C under IR irradiation and immediately placed in contact under a pressure of 0.8MPa for 12 seconds. Adhesion was measured 72 hours after joint formation in an Instron 4411 universal testing machine (Instron Ltd., Buckinghamshire, UK) by using a peeling rate of 100 mm/min. Five replicates for each adhesive joint were used. The error was ± 0.7 kN/m. For precise assessment of the locus of failure in the joints, the failed surfaces obtained after T-peel test were analyzed using ATR-IR spectroscopy and SEM.

2.2.7. Adhesion of tape/paint/EVA joints. Acrylic paint was brushed on the as-received and UV-ozone treated EVA (150 x 30 x 2 mm³) and the thickness was adjusted by means of a metering rod of 150 µm. After allowing the paint to dry for 24 hours, the rubber tape was applied and pressed with a rubber roller 20 times. T-peel tests in tape/paint/EVA joints were carried out 72 hours after joint formation in a TA-XT2i texture analyzer (Stable Microsystems, Surrey, UK) by using a peeling rate of 150 mm/min. Five replicates were tested and the results averaged.

3. RESULTS AND DISCUSSION

3.1. Characterization of the EVAs treated with UV-ozone

Water advancing contact angles were measured on EVA surfaces immediately after UV-ozone treatment. Figure 1 shows high water contact angle values for the as-received EVA12 (94 degrees) and EVA20 (83 degrees) indicating low wettability, and the water contact angle decreases by increasing the VA content. The treatment with UV-ozone decreases moderately the water contact angle values up to a length of treatment of 5 minutes being almost similar for more

extended duration of the treatment; the incidence of the UV-ozone treatment in increasing the EVA wettability is more marked in EVA12.

ATR-IR and XPS spectroscopy were employed to analyze the chemical changes in the EVA surfaces after UV-ozone treatment. Figure 2 shows, as a typical example, the ATR-IR spectra of the as-received and UV-ozone (7.5 minutes) treated EVA20. The ATR-IR spectrum of the as-received EVA20 shows the typical bands of vinyl acetate at 1739, 1242, 1023 and 606 cm^{-1} , and ethylene at 2919, 2846, 1467, 1375, and 725 cm^{-1} . Higher increase of the relative intensity of the bands due to VA can be noticed more by increasing the vinyl acetate content in EVA. UV-ozone treatment for 7.5 minutes decreases the intensity and increases the width of the band at 1739 cm^{-1} due to C=O of vinyl acetate, indicating the formation of new carbon-oxygen moieties on both treated EVA surfaces. Similar results [22,23] were found for polyethylene treated with UV-ozone indicating that oxidation of ethylene units are produced. The formation of new carbon-oxygen moieties in the EVAs treated with UV-ozone can be better evidenced by the ratio of the intensities of the bands due to vinyl acetate (1740 cm^{-1}) and ethylene (2916 cm^{-1}). According to Table 2 the UV-ozone treatment decreases that ratio because of the oxidation of the ethylene in the EVA, more markedly by increasing the length of treatment.

XPS, a more sensitive surface analysis technique, was used to assess the chemical modifications produced on the outermost EVA surfaces treated with UV-ozone. The as-received EVAs are mainly composed of carbon (95.2at% and 93.7at% in EVA12 and EVA20, respectively). The O/C ratios (Table 3) on the as-received EVAs are lower than expected according to their stoichiometric composition (0.11 for EVA12 and 0.17 for EVA20) likely due to the heterogeneous distribution of the vinyl acetate into the copolymer. According to Table 3, EVA12 needs more than 5 minutes of UV-ozone treatment for noticeable modification of its surface chemistry; however, EVA20 only needs one minute treatment with UV-ozone. Longer duration of UV-ozone treatment does not cause important changes on the surface chemistry of the EVAs and in fact the UV-ozone treatment for 7.5 minutes produces similar surface oxidation levels in both EVAs.

As a typical example, the curve fitting of the C1s photopeak of the as-received and UV-ozone treated EVA20 is shown in Figure 3a. The oxidation caused by UV-treatment is evidenced by the new bands at binding energies of 286.6,

288.0 and 289.2 eV due to C-O, C=O and -COO moieties respectively. Figure 3b shows that the UV-ozone treatment causes a decrease in the content of C-C and C-H species (285.0 eV) and an increase in the amount of C-CO/C-C groups in polyethylene, C-O and -COO moieties (binding energies at 285.6, 286.6 and 289.2 eV, respectively) in both EVAs. Furthermore, the UV-ozone treatment also creates C=O groups (binding energy : 288.0 eV [24]), in agreement with the results obtained by ATR-IR spectroscopy. The treatment of both EVAs with UV-ozone during 1 minute is sufficient to oxidize their surfaces particularly in EVA 20.

SEM micrographs (Figure 4) of the as-received EVA surfaces reveal surface markings which can be attributed to the injection process. UV-ozone treatment during 1 minute causes smoother surfaces but for longer lengths of treatment (5 min) some cracks are created on the EVA12 surface and ablation is dominant on the EVA20 surface. UV-ozone treatment for 7.5 min causes ablation mainly in both EVAs. The dominant ablation on the EVA20 surface can be ascribed to the different mechanical properties of the VA and ethylene units, as the lower mechanical properties of the VA with respect to ethylene may justify the early ablation of EVA20.

The incidence of the UV-ozone treatment on the roughness in the nano scale of the EVAs was studied by AFM. Due to the high heterogeneity of the EVA surfaces, an area of $20 \times 20 \mu\text{m}^2$ was analyzed. Figure 5 reveals a greater level of fine detail roughness on the EVA20 surface, both for the as-received and UV-ozone treated during 7.5 min; this similarity in roughness confirms the dominant ablation on the EVA20 surface for long UV-ozone treatment. However, coarser roughness and deeper crests are found on the as-received EVA12 than on EVA20 and treatment with UV-ozone increases more the roughness of EVA12.

3.2. Adhesion of the UV-ozone treated EVAs

Adhesion assessments of the UV-ozone treated EVAs was obtained from T-peel tests of as-received and UV-ozone treated EVA/polychloroprene adhesive+5wt% polyisocyanate adhesive joints. The joint made with the as-received EVA12 shows very low T-peel strength because of its low surface energy (Figure 6). However, the joint made with as-received EVA20 is higher, likely due to the swelling produced by the solvent composition in the polychloroprene adhesive which should favour the diffusion of polymer chains

on the surface between the EVA20 and the polychloroprene adhesive. The treatment with UV-ozone for 1 min increases the peel strength of the joints made with both EVAs, the adhesion is higher in the joints made with EVA20. On the other hand, the highest T-peel strength value in the joints made with EVA12 is obtained by UV-ozone treatment for 5 min whereas for the joints made with EVA20 the adhesion decreases slightly by increasing the length of treatment. These trends can be better explained by analysing the loci of failure of the joints.

The loci of failure of the adhesive joints were assessed by analyzing the failed surfaces after peel test using ATR-IR spectroscopy (Figure 7) and SEM (Figures 8a, 8b and 8c). The ATR-IR spectrum of the polychloroprene + 5wt% polyisocyanate adhesive shows the typical bands of =C-H stretching of aromatic ring (3025 cm^{-1}), C-H stretching of methylene groups (2930 and 2867 cm^{-1}), C=C stretching (1660 cm^{-1}), C-Cl stretching (830 cm^{-1}), aromatic-COOH of the tackifier (1745 cm^{-1}), and asymmetric stretching due to the N=C=O group of the isocyanate (2269 cm^{-1}). The failed surfaces of the joints made with the as-received EVAs (Figure 7 shows the ATR-IR spectra of the joint made with the as-received EVA20 as a typical example) show an adhesion failure, i.e. one of the failed surfaces corresponds to the adhesive (A surface) and the other corresponds to the EVA surface (P surface). However, the SEM micrographs of Figure 8a show some deformation on the failed P surface due to EVA20 and/or the adhesive layer, likely due to the softening and swelling of EVA20 by the solvents in the polychloroprene adhesive. On the other hand, the analysis of the failed surfaces in the joints made with UV-ozone treated EVA show different locus of failure. The ATR-IR spectra of the failed surfaces made with UV-ozone treated EVA20 for 7.5 min (taken as a typical example) are given in Figure 7. The ATR-IR spectrum of the A surface exhibits bands typical of both the EVA20 and the adhesive, whereas the ATR-IR spectrum of the P surface corresponds to EVA20. Furthermore, the SEM micrographs of the failed surfaces in the joints made with EVA treated with UV-ozone during 5 minutes (Figure 8b) and 7.5 minutes treatment (Figure 8c) show the presence of bubbles in the adhesive on the failed A surface and peeled crevices of EVA on the failed P surface, indicating a mixed failure of adhesion and cohesive failure in a thin EVA layer, likely caused by the formation of a weak boundary layer on the UV-ozone treated EVA surface. On the other hand, for the joints made with EVA12, the

failure in the P surface is more cohesive in the EVA when it is treated with UV-ozone during 5 minutes than during 7.5 minutes, confirming the favoured formation of a weak boundary layer in the joints made with EVA12 with respect to EVA20; this locus of failure supports the decrease in peel strength showed in Figure 6 for the joint made with EVA12 treated with UV-ozone for 7.5 minutes.

By considering the evidence obtained from the peel strength values and the locus of failure of the joints, it can be concluded that for EVA12 the adhesion increases by increasing the length of UV-ozone treatment up to 5 minutes because the creation of surface polarity and roughness; longer length of treatment causes ablation and mechanical weakening of the surface leading to the formation of a weak boundary layer which is detrimental to adhesion. However, for the joints made with UV-ozone treated EVA20, a cohesive failure is obtained for short lengths of treatment due to the easier and earlier creation of the weak boundary layer.

The adhesion of the UV-ozone treated EVAs to acrylic paint were also tested. The peel strength values of tape/paint/EVA joints given in Figure 9 show that all joints exhibit similar peel strength values and an increase in the joint made with UV-ozone treated EVA20 for 5 min is obtained only. Furthermore, the loci of failure in these joints were different. The joints made with the as-received and UV-ozone treated EVA12 for 1 and 5 min, and the joints made with the as-received and UV-ozone treated EVA20 for 1 min, show an adhesion failure between the paint and the EVA surface, i.e. the paint is removed from the EVA surface. Only the joint made with UV-ozone treated EVA20 for 5 min shows an adhesion failure between the adhesive tape and the EVA surface, i.e. the paint is well adhered to the EVA.

The ageing of the UV-ozone treated EVA/polychloroprene adhesive joints was tested by placing the adhesive joints in a weathering chamber at 50°C and 95% relative humidity for 72 hours. The T-peel strength values obtained after ageing (Figure 10) shows similar trend than in the joints before ageing. In general, the peel strength values increase after ageing likely due to additional cross-linking of the polychloroprene adhesive under temperature.

3.3. Durability of the surface modification on the UV-ozone treated EVAs

The surface modifications on polymers produced by UV treatment creates unstable short-life species that can be lost with time [8,11]. Therefore, the

duration of the surface modifications on the UV-ozone treated EVAs was analyzed. The UV-ozone treated EVAs for 7.5 min (in which a cohesive failure in the adhesive joints was obtained) was kept under open air laboratory conditions and the variations of their surface properties were studied over time after treatment.

Advancing water contact angle values (Figure 11) on the UV-ozone treated EVAs remain almost constant by increasing the time after treatment and they are always lower than on the as-received polymers, indicating that the surface modifications of the UV-ozone treatment remain on the EVA surfaces for 24 hours after treatment at least. The surface chemistry on the UV-ozone treated EVAs was monitored by XPS (Tables 5 and 6). The O/C ratio on the treated EVAs remains constant for at least 24 hours after treatment. Moreover, a slight increase in oxygen content is found (increase in the content of C-CO, C-O and COOR moieties, Table 6) particularly in the UV-ozone treated EVA20, likely due to the reaction of the surface species on the EVA with oxygen and/or moisture in the air. However, although the surface modifications on both treated EVAs are maintained for 24 hours after treatment, the T-peel strength values obtained in joints made at different times after UV-ozone treatment decrease, irrespective of the VA content in the EVA. Consequently, other factors should be responsible for the loss of adhesion of the UV-ozone treated EVAs by increasing the time after treatment.

It is known the high solubility of polar species into polar solvents. In fact, previous studies [25] have shown the dissolution of the polar groups created on the surface of rubber materials treated with plasma by application of organic solvents. The solvent born polychloroprene adhesive used in this study contains toluene, ethyl methyl ketone and n-hexane and there is the possibility of removal of the polar moieties created by UV-ozone treatment on EVA surfaces in the presence of these organic solvents. Therefore, EVA specimens treated with UV-ozone for 5 min were wiped with a mixture (1:1:1 v/v) of toluene, ethyl methyl ketone and n-hexane. After allowing 72 hours for evaporation under open air (the same time used between the application of the adhesive and the T-peel test in the adhesive joints), the surface chemistry of the EVAs was studied by XPS. According to Table 6, solvent wiping decreases the O/C ratio and increases the carbon content on the EVA surfaces, mainly on the UV-treated EVA20, indicating that the decrease in peel strength values in the

adhesive joints can be ascribed to the removal of surface groups on the EVA by the organic solvent mixture in the polychloroprene adhesive.

4. CONCLUSIONS

UV-ozone treatment enhanced the wettability, created new carbon-oxygen moieties, and increased the roughness on the surfaces of EVAs containing 12 and 20wt% vinyl acetate. EVA12 showed less surface chemistry modification and greater roughness. UV-ozone treatment for 1 (EVA20) and 5 min (EVA12) gave the highest increase in adhesion of EVAs to polychloroprene adhesive. Longer UV-ozone treatments generated the creation of a weak boundary layer on the EVA surfaces in which the failure occurred during peel tests. On the other hand, effective adhesion to acrylic paint was obtained with UV-ozone treated EVA20 for 5 min. The ageing resistance of the adhesive joints was quite good and the extent of the surface modifications of the UV-ozone treated EVAs lasted for at least 24 hours after treatment. However, the peel strength values of the adhesive joints decreased by increasing the time after UV-ozone treatment likely due to the removal of the polar moieties on the EVA surfaces by the organic solvents contained within the adhesive.

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Table 1. Some properties of the EVA copolymers used in this study [19].

Copolymer	VA (wt%)	MFI* (g/10 min)	Shore hardness	
			A	D
EVA12	12	0.6	96	45
EVA20	20	3.0	91	39

*Melt flow index

Table 2. Ratio of the intensities of the ATR-IR bands at 1740 and 2916 cm^{-1} of as-received and UV-ozone treated EVAs.

Length of treatment (min)	I_{1740}/I_{2916}	
	EVA12	EVA20
0	0.67	0.98
1	0.69	0.88
5	0.51	0.61
7.5	0.44	0.62

Table 3. Chemical composition and O/C ratio values on the as-received and UV-ozone treated EVAs. XPS experiments.

EVA12

Length of treatment (min)	Percentage (at%)		O/C
	C	O	
0	95.2	4.8	0.05
1	95.2	4.8	0.05
5	92.8	7.2	0.08
7.5	89.8	10.2	0.11

EVA20

Length of treatment (min)	Percentage (at%)		O/C
	C	O	
0	93.7	6.3	0.07
1	90.8	9.2	0.10
5	89.6	10.3	0.11
7.5	90.0	10.0	0.11

Table 4. Chemical composition on the as-received and UV-ozone treated EVAs for 7.5 min as a function of the time after treatment.

EVA12

Time after UV-ozone treatment	Percentage (at%)			O/C
	C	O	N	
As-received	95.2	4.8	---	0.05
UV-ozone – 0 min	91.7	7.8	0.5	0.09
UV-ozone – 30 min	91.1	8.4	0.5	0.09
UV-ozone – 1440 min	91.6	7.8	0.6	0.09

EVA20

Time after UV-ozone treatment	Percentage (at%)			O/C
	C	O	N	
As-received	93.7	6.3	---	0.07
UV-ozone – 0 min	91.7	7.9	0.4	0.09
UV-ozone – 30 min	90.7	8.9	0.4	0.10
UV-ozone – 1440 min	90.7	8.9	0.4	0.10

Table 5. C1s species on the as-received and UV-ozone treated EVAs for 7.5 min as a function of the time after UV treatment.

EVA12

	Percentage (at%)				
Chemical species	C-C, C-H	C ⁺ -CO ó C-C in polyethylene	C ⁺ -O	C=O, NH-CO	(C ⁺ =O)-O
Binding energy (eV)	285.0	285.6	286.6	288.0	289.2
Time after treatment					
As-received	84.8	8.0	6.1	---	1.1
UV-ozone – 0 min	77.5	9.8	10.0	1.5	1.2
UV-ozone – 30 min	74.8	11.4	11.3	1.0	1.5
UV-ozone – 1440 min	74.6	11.6	11.7	0.6	1.5

EVA20

	Percentage (at%)				
Chemical species	C-C, C-H	C ⁺ -CO ó C-C in polyethylene	C ⁺ -O	C=O, NH-CO	(C ⁺ =O)-O
Binding energy (eV)	285.0	285.6	286.6	288.0	289.2

Time after treatment					
As-received	76.2	11.6	10.6	---	1.6
UV-ozone – 0 min	78.2	9.1	9.8	1.3	1.6
UV-ozone – 30 min	74.2	11.5	11.2	1.2	1.9
UV-ozone – 1440 min	65.3	17.3	15.2	---	2.2

Table 6. Chemical composition on the UV-ozone treated EVAs during 5 min before and after solvent wiping.

EVA12 – UV-ozone 5 min	Percentage (at%)			O/C
	C	O	N	
Before cleaning	91.3	7.6	1.1	0.08
After cleaning (toluene + ethyl methyl ketone + n-hexane)	92.1	7.7	0.2	0.08
EVA20 – UV-ozone 5 min	C	O	N	O/C
Before cleaning	91.3	8.1	0.6	0.09
After cleaning (toluene + ethyl methyl ketone + n-hexane)	95.5	3.5	1.0	0.04

FIGURE CAPTIONS

Figure 1. Variation of the water advancing contact angle values on as-received and UV-ozone treated EVAs as a function of the length of treatment.

Figure 2. ATR-IR spectra of the as-received and UV treated (7.5 min) EVAs.

Figure 3a. Curve fitting of C1s photopeak on as-received and UV-ozone treated EVA20.

Figure 3b. Chemical composition (at%) of species on as-received and UV-ozone treated EVAs. Curve fitting of C1s photopeak.

Figure 4. SEM micrographs of the as-received and UV-ozone treated EVAs. Magnification : x3000

Figure 5. AFM images of the as-received and UV-ozone treated EVAs.

Figure 6. T-peel strength of as-received and UV-ozone treated EVA / polychloroprene + 5wt% polyisocyanate adhesive joints.

Figure 7. ATR-IR spectra of the failed surfaces obtained after T-peel test of the as-received and UV-ozone treated (7.5 min) EVA20 / polychloroprene + 5wt% polyisocyanate adhesive joints.

Figure 8. SEM micrographs of the failed surfaces obtained after T-peel test of the **a)** as-received, **b)** UV-ozone treated (5 min) and **c)** UV-ozone treated (7.5 min) EVA/polychloroprene + 5wt% polyisocyanate adhesive joints. Magnification : x500

Figure 9. T-peel strength values of tape/paint/as-received and UV treated EVA joints.

Figure 10. T-peel strength values of as-received and UV-ozone treated EVA/polychloroprene + 5 wt% polyisocyanate adhesive joints before and after ageing (50°C - 95% relative humidity - 72 h).

Figure 11. Variation of the advancing water contact angle values on UV-ozone treated EVAs for 7.5 min as a function of the time after treatment.

Figure 12. T-peel strength of as-received and UV-ozone treated EVA for 7.5 min/polychloroprene + 5 wt% polyisocyanate adhesive joints as a function of the time after treatment.

Figure 1

Figure 2

EVA20 **Figure 3a****F**

Figure 4

EVA12

EVA20

As-received

UV-7.5 min

Figure 5

Figure 6

Figure 8a

Figure 8b

Figure 8c

Figure 9

Figure 10

Figure 11

Figure 12