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Improvement of acrylic-urethane paint adhesion to PP-EPDM surface by mediated electrochemical oxidation

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Abstract. Adhesion improvement of acrylic-urethane paint on bumper surface made of polypropylene/ethylene-propylene-diene monomer was investigated in the long term after electrochemical treatment by 2N nitric acid and 0.6M silver (II)-nitrate/2N nitric acid. The stability of electrochemically treated samples was examined at different aging times by ATR and SEM. The results were also compared to those of untreated and flame-treated samples. Accelerated UV weathering analysis and morphological study by SEM confirmed the effectiveness of the Ag (II) treatment technique in the long term, particularly at the curvature of the bumper. For the Ag (II)-treated samples, increase in adhesion strength was sustained even after 650 hours of exposure to UV irradiation in wet conditions before bonding. In addition, the stability of the Ag (II)-treated surface was maintained for at least three months. In the case of the flame-treated surface, hydrophobic recovery during aging in the environment was found to reduce the polarity of the PP-EPDM surface. The pull-off test showed that Ag (II) treatment could enhance the adhesion strength of the acrylic-urethane coating onto PP-EPDM in comparison with the flaming method by 20.7%. Moreover, the results of zeta potential analysis for Ag (II) treated blend showed a typical acidic surface.

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1. Introduction

A major problem with utilizing polypropylene (PP), widely used as the main body of auto bumpers, is its non-polar surface, which in turn, makes its wetting property and paint adhesion poor in quality [1,2]. Different surface modification techniques have been applied to improve the wetting characteristics of such non-polar plastics. These include chemical treatment by environmentally hazardous chemicals such as trichloroethylene [3], corona discharge with high frequency and voltage [4,5], plasma treatment in vacuum [6,7], air plasma [8,9], flame treatment with little prospect for irregular shapes [10,11], and recently proposed mediated electrochemical treatment [12,13]. Among these techniques, the boosting electrochemical treatment is considered to be an effective method to amplify the surface energy of the plastics and improve their adhesion to other layers. Polyolefin is among the most regularly surface-modified polymers for this purpose. Brewis et al. [3,14,15] investigated the possibility of applying electrochemical techniques for the

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modification of polyolefin such as PP and polyethylene (PE) over the last decade. They found that the mediated electrochemical treatment was more efficient in terms of joint strength for PE than PP. Their results also revealed that the concentration of oxygen formed on PP surface was limited to about 4 atom% [16]. We have also recently reported the effectiveness of Mediated Electrochemical Oxidation (MEO) by Ag (II) ions as a substitute for the conventional flame-treatment technique for the modification of PP/EPDM bumper. Initial results show that MEO by Ag (II) offers an attractive opportunity for increasing surface polarity of non-polar polymer alloys [17]. It has recently been reported that surface modification of some rubbers, e.g., BR, NR, and EPDM by MEO, improves their surface characteristics for compatibility with other materials in blending [18–20]. Electrochemical surface modification of the non-polar plastics such as PE, PP, and PS [3], rubbers such as BR and NR [14], SBR [15], and BR-clay nanocomposite [18] has already been reported in the literature. However, the surface aging and adhesion strength of electrochemically modified polymers have yet to be addressed. To obtain a deeper understanding of Ag (II) treatment on the chemical and physical nature of the surface, aging and adhesion strength of PP-EPDM blend were thus studied after exposure to an accelerated UV irradiation test in a wet condition. Since surface properties may change with time upon storage in atmospheric conditions, chemical changes in the PP-EPDM surface have also been tracked for three months. Aging study was followed by ATR, EDX, and contact angle measurements. The results were also compared to those of the untreated and flame-treated PP-EPDM sheets.

A growing desire to minimize painting of automotive parts is increasing the necessity for reliable predictions of weathering performance. Accelerated UV weathering analysis is a useful technique that provides relatively quick responses to color change and surface resistance after exposure to heat, cold, UV, moisture, and high temperature. This technique is vital to examine any possible damage to the treated surface caused by sunlight, rain, and moisture, particularly at the curvature of bumpers. Therefore, all PP-EPDM samples were initially coated with the same acrylicurethane paint. Then, accelerated UV weathering and surface characterization techniques were employed to investigate the effectiveness of Ag (II) treatment. The study of the low accessible area of PP-EPDM bumper was our main interest.

2. Experimental

2.1. Materials

Silver (I)-nitrate and nitric acid were obtained from Sigma-Aldrich and Merck Inc., respectively. PP-EPDM bumper plates (polypropylene/ethylenepropylene-diene monomer blend) with a thickness of 3.0 mm were supplied by Kimia Baspar Company, Iran. The blend weight formulations were: 76% PP, 19% EPDM, and 5% talc-filled and other additives such as Nano and carbon black. The melt flow index of PP at 230°C was 12 g/10 min. It has a density of 0.9 g/cm³. The EPDM contains 57 wt% of ethylene and 4.5wt% of ethylidene norbornene. It has a Mooney viscosity (MU₁₊₄ at 125°C) rate of 77.

The curvature area of the bumper was cut into small pieces $(2 \times 2 \text{ cm}^2)$ and cleaned in 2-propanol according to the factory procedure. The paint included thermoplastic acrylic (Trade number: PL 2181) and acrylic-urethane (Trade number: PL 7040) purchased from Goharfam Co., Iran as the primer and the base coat, respectively. The thickness of the paint including the primer and base coats was 35 μ m.

2.2. Treatment techniques

The electro-oxidation of Ag (I) in an electro-membrane cell was performed using IrO_2/Ti DSA anode, Ti cathode, and Ag/AgCl reference electrode. The anolyte included AgNO₃ in 7 N HNO₃ media and catholyte included HNO₃ 8 N (Figure 1). Nafion[®] 115 membrane was employed as a separator. Constant cell voltage (2.2–2.8 V) was applied to the cell during electrolysis by PGSTAT30 system (Eco Chemie Autolab) which fitted



Figure 1. Schematic diagram of the electro-membrane cell used in this study [19].

with the General Purpose Electrochemical Software (GPES). After cleaning the samples with a 2-propanol solution, the electrochemical treatment with dilute nitric acid (2N) or in the presence of Ag (II) ions under optimum conditions obtained previously [21] was carried out in an electro-membrane cell.

The pieces of bumper sheet were placed in the anolyte adjacent to the anode at the contact time of 5 to 15 min.

Fuel for flame treatment was butane (C_4H_{10}), and air/fuel-ratio was 22/1. Flame gun height was about 25–250 mm. For flame treatment, a gas burner was passed at 3 cm above the PP-EPDM sheets at a speed of flame set at 400 mm/s. The operating condition for flame treatment was fixed according to the procedure described by [22].

2.3. Test methods

2.3.1. Atomic Force Microscopy (AFM)

A commercial AFM (Dualscope/Rasterscope C26, DME, Herlev, Denmark) was carried out for examining the surface topography and roughness of different treated samples in various scan areas. All analyses were performed at room temperature with a relative humidity rate of 50%. The roughness parameters selected as the maximum height and the RMS data were determined using average of surface height values. The AFM measurements were achieved in three different places for each blend.

2.3.2. IR-ATR absorption spectroscopy

IR-ATR technique was employed to characterize the chemical structure of the samples. The spectral resolution of ATR/FTIR spectrophotometer (Equinox 55, Bruker, Germany) was 4 cm^{-1} . Wave numbers ranging from 400 to 4000 cm⁻¹ were recorded as a function of transmittance.

2.3.3. Scanning Electron Microscopy (SEM)

Surface morphology of the samples was examined by SEM (Brno, Czech Republic) which worked in the secondary electron mode at 20 kV.

2.3.4. Energy dispersive X-ray analyses (EDXA)

Oxygen-element mapping was also used by SEM equipped with energy dispersive X-ray analysis (EDXA). The sheets were mapped in the secondary electron mode at 10 kV.

2.3.5. UV accelerated analysis

UV accelerated analysis was carried out according to ASTM D4587-11 for testing automotive coating. According to this test method, the ability to paint samples with different treatments is compared with that with the untreated sample. In this way, one can investigate how a painted sample may resist deterioration in terms of physical and optical properties caused by exposure to light, heat, and moisture. The experimental conditions were set according to the procedure described in ASTM D4587-11, as mentioned in Table 1.

2.3.6. Contact angle measurement

The surface wettability of the PP-EPDM blend sample was determined by static contact angle measurements (error $\pm 5\%$) with sessile drop technique using the surface energy evaluation system (KRUSS G10, Germany) [14,17]. The measurements of the water contact angles (error $\pm 5\%$) were also performed using distilled water at 10 different positions. For reproducibility confirmation, each liquid probe was carried out five times, the mean value of which was reported.

2.3.7. Zeta potential measurements

The zeta potential (isoelectric point: IEP) of different treated PP-EPDM samples was measured in the pH range of 3–12 using Electro kinetic analyzer (EKA SurPass-type A, Anton Paar GmbH, Graz, Austria). The EKA system is composed of an automatic pH titrator with an evaluation software program and a temperature sensor.

2.3.8. Pull-off test

Pull-off adhesion test was performed according to ASTM D5179. To carry out pull-off tests, aluminum dollies adhered to the surface of the coated samples and, then, were left for at least 24 h to be fully cured. Afterward, by a 5 kN universal testing machine, the fixture was strained at a rate of 1 mm/min until the adhered dollies were removed from the substrate with the maximum recorded load. Finally, the force trends versus extension were recorded by the tensile machine. For each mode, six replicated samples were performed and, then, the mean values were reported.

Table 1. UV-condensation exposure t	test
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Cycle description	340 nm irradiance	Black panel temperature	Relative humidity	Typical uses
8 hUV,	$0.83 \text{ W}/(\text{m}^2 \text{ nm}) \text{ dark}$	$70 \pm 2.5^{\circ}C$		Automotive
4 h condensation,	period	$50 \pm 2.5^{\circ} C$	$50 \pm 5\%$	coatings
repeated continuously	1			0

3. Results and discussions

3.1. Chemical structure of surface aging

Surface micro hardness of the electrochemically treated PP-EPDM samples was investigated, and the results were compared to those of the untreated sample. A comparison of the surface topography of the untreated and Ag (II)-treated samples clearly shows the etching ability of the electrochemical treatment technique (see Figure 2 and Table 2.). The untreated sample has a comparatively smoother surface, whereas the Ag (II)-treated sample shows a uniform chemically etched surface, leading to a considerable change in topography by treatment. Rq is characterized by a value of 136 for the Ag (II) compared to 139 nm for the untreated sample. Surface roughness in the Ag (II)treated sample has slightly increased mainly due to the enhanced effective surface area and the formation of more edge sites, leading to the higher adsorption of the polar groups on these active sites and a better mechanical interlocking.

The ATR absorption on the surface layer of the PP-EPDM sheets before bonding with the paint was measured one day after electrochemical treatment by Ag (II) ions and then again after three months. The results, which have been compared to those of the untreated PP-EPDM samples, are depicted in Figure 3. As evident, on the surface of the treated sample by Ag (II) in comparison with the untreated sheet, a new absorption peak within the wavelength range of 1650 to 1660 cm⁻¹ has appeared after 1 day, which is attributed to the polar carbonyl groups in an oxidizing

medium [23,24]. Besides, a strong wide absorption band for the Ag (II)-treated surface is observed at about 3080 to 3685 cm⁻¹, which may be associated with the presence of both hydroxyl and carboxyl groups [6]. However, a decrease in the intensity of the bands at 3485 cm⁻¹ after 3-month storage is observed. The strong and intense peak at about 1665 cm⁻¹ indicates the presence of a carboxylic acid or carbonyl group after 1 day and 3-month storage periods for the Ag (II)-treated samples. This means that the new active sites are perhaps associated with the surface etching caused by the electrochemical treatment [17].

In addition, the intensive absorption peaks at 1261, 1041, and 1099 cm⁻¹ are noticeable, particularly after 1-day storage, which is attributed to -C-O stretching bands and the formation of ester bands within the wave number range of 900 to 1300 cm⁻¹ [25]. During the first 3 months, the peak intensities for Ag (II)-treated sample decreased quite slowly. The reason for oxidizing the surface properties after ambient aging may be the reactive unsaturation and oxidized hydrocarbons in the absorption band range of 1650 and 3300 cm⁻¹ [16,25].

Figure 4 depicts surface oxygen content obtained from EDX spectra of the untreated PP-EPDM sheet before bonding with the paint compared to the electrochemically treated samples by Ag (II), nitric acid (2N), and flame at different aging times. As seen earlier, various oxygen-containing functional groups







Figure 3. ATR-IR spectra of Ag (II) treated PP-EPDM sample in comparison with the untreated one at different aging times.

Table 2. The roughness parameters for PP-EPDM untreated and electrochemically treated samples.

Samples	Untropted	Electrochemically	
Samples	Ontreated	treated by Ag (II)	
Root-mean square roughness $(R_q: nm)$	136 ± 1	139 ± 0.9	
Mean square roughness $(R_a: nm)$	91 ± 1.1	98 ± 0.7	
S_{dq}	0.28	0.27	

appeared particularly on the surface of the Ag (II)treated sample, leading to the significant enhancement of oxygen content (18.28%) in comparison with the untreated (5.7%) and flame-treated (10.05%) samples after one-day storage time. However, prolonging storage time to three months caused a slight decrease in the introduced polar groups containing oxygen. The presence of surface functional groups is more distinct for the electrochemically treated samples, particularly for the one modified by Ag (II).

Although the oxygen content for the flame-treated sample has somewhat increased, the surface exhibits rather more changes upon aging. As is evident, the oxygen content of the flame-treated sample decreased more than those of the electrochemically treated ones after three months. It appears that once treated by Ag (II) ions, PP-EPDM surface will have a more stable surface, which is favorable in the long term due to measured oxygen content and characterized functional groups.

The effect of electrochemical treatment on the

wettability of the PP-EPDM surface before bonding with the paint was also investigated, and the results were compared to those of the untreated and flametreated samples. The results of contact angle measurements at different ambient aging times were thus obtained and depicted in Figure 5. As observed earlier, the contact angle of the flame-treated sample decreased more than that of the untreated one; however, in the course of aging, contact angle increased again significantly. This may be caused by the reorientation of functional groups into the surface layer of the blend sheet [17]. The treatment of PP-EPDM surface by electrochemical technique, particularly for the Ag (II)treated samples, resulted in a considerable decrease in the water contact angle so that the long-term aging could not cause a significant loss in wettability. This observation strongly suggests that the wettability or contact angle on the Ag (II)-treated PP-EPDM sample appears not time dependent. The results also suggest that Ag (II) treatment may lead to proper surface etch-



Figure 4. Surface oxygen content of PP-EPDM sheets treated by different techniques as a function of aging time.



Figure 5. Water contact angle for PP-EPDM samples treated by different techniques as a function of aging time.

ing and possibly long-term adhesion strength, which will be discussed in the next section.

3.2. UV accelerated analysis

As found earlier [17], the electrochemical pretreatment could create polar groups on a polymeric surface, leading to increased surface energy. Consequently, the wettability and adhesion of the paint to the polymeric surfaces have improved through polar-polar interactions. However, there can be two more potential problems. First is the aging problem in atmospheric conditions, as discussed in the previous section. The second one is adhesion failure in a real environment under wet conditions, light exposure, and so on. Therefore, by means of UV accelerated analysis, the adhering system between the primer coat and the surface-treated PP-EPDM by different methods in the curvature area was evaluated using strong UV irradiation in a wet environment. The results were also compared to those of the untreated sample. For rapid acceleration of the tests, UV-B test method was used according to ASTM D4587-11, which accelerated the degradation process. Figure 5 shows different treated samples particularly in the curvature area, which were coated by the same thermoplastic acrylic and acrylic-urethane as the primer and base coats, respectively. According to Figure 6(a), the surface of all samples including those painted before UV exposure is visually detect free. The UV analysis results after 90 hours (Figure 6(b) showed that there was much more yellowing resistance against color change during the exposure in the electrochemically treated samples (3 and 4) than the untreated or the flame-treated ones (1 and 2). This effect is more distinct upon increasing the UV accelerated time so that after 160 and 650 hours of UV radiation (B) (weathering) (Figure 6(c) and (d)), the Ag (II) treatment can help attenuate the color change (sample c). Since the same coating was applied to the surface of each sample with uniform thickness (35 microns), different outcomes may be attributed to the surface chemistry and type of modification. It appears that in accelerated conditions, gas diffusion by O_2 , nitrogen, and SO_2 occurs easier and faster from surface to depth. Further, the chemical reaction between aromatic rings at the interface of the substrate and base coat occurred as a result of chromophoric reactions, which is the main cause of discoloration [26,27]. Apparently, on the untreated surface, due to insufficient mechanical interlocking between surface and base coat, more discoloration is observed.

These observations are in good agreement with earlier studies for polyurethane degradation after UV irradiation. Yousif et al. [28] recently considered the surface degradation of polymers by exposure to UV irradiation. They reported that UV irradiation caused oxidative degradation that produced free radical and



(1) Untreated,

(2) Flame treated,

(3) Electrochemically-treated by Ag (II) in optimum condition,

(4) Electrochemically-treated by 2 N HNO_3)

Figure 6. UV accelerated test for acrylic-urethane coating according to ASTM D4587-11 on the PP-EPDM samples treated by different methods: (a) Before UV exposure, (b) after 90 hr of UV exposure, (c) after 160 hr of UV exposure, and (d) after 650 hr of UV exposure analysis.

caused the deterioration of mechanical properties, thus leading to the production of useless materials. When a polymer is subjected to UV irradiation, it undergoes rapid yellowing. Many factors are responsible for the discoloration of polymeric materials such as internal and external impurities, which may contain chromophoric groups. Similarly, Rosu et al. [28] investigated the vellowing of polyurethane as a result of UV irradiation. Based on their results, the photochemical degradation of polyurethane is associated with the scission of the urethane group, and these reactions are combined with the yellowing of the polyurethane surface. It was concluded that, after UV irradiation, the oxidation of the central methylene group with quinone formation caused yellowing as a result of chromophoric reactions.

3.3. Adhesion strength of surface in the curvature area after UV accelerated by SEM

After the removal of the coated PP-EPDM samples from accelerated environmental conditions, SEM images were taken to investigate the strength of junctions between the curvature surface and the primer. Thus, all samples were cut cross-section in liquid nitrogen, and the junction between surface and primer coating was evaluated at different magnifications. Figure 7 shows the untreated PP-EPDM surface junction with acrylic urethane coating after 650 hours of exposure to the UV accelerated conditions at two magnifications of 500 and 1000 times. As is evident, a noticeable separation with a thickness rate of 5.69 micron can be seen in large areas at the junction coating on the surface. This induces no appropriate strength on the untreated surface after exposure to UV accelerated conditions. Cross-sectional view of the SEM micrographs for the acrylic-urethane coating on the flame-treated sample after 650 hours of UV exposure at different magnifications is shown in Figure 8. As is obvious, there is better strength at the interface between the PP-EPDM surface and the primer coating, though a gap with 550 nm thickness shows the lack of appropriate strength in this junction. These results reveal that the bond between the primer and the flame-treated surface is highly vulnerable to moisture attack and gas diffusion.

Figure 9 illustrates SEM micrographs at the crosssection of the Ag (II)-treated sample after exposure to



Figure 7. Cross-sectional view of the SEM micrographs (magnifications $500 \times$ and $1000 \times$) for the acrylic-urethane coating on the untreated PP-EPDM sample after 650 hours of exposure to accelerated conditions (surface thickness: 34.81 μ m).



Figure 8. Cross-sectional view of the SEM micrographs (magnifications $700 \times$ and $20000 \times$) of the acrylic-urethane coating on the flame-treated PP-EPDM sample after 650 hours of exposure to UV accelerated conditions (surface thickness: 34.78 μ m).

UV accelerated conditions for 650 hours. Evidently, at the junction of primer coating, even at the high zoom level measured by SEM (20000 X), there is no groove and connection between the substrate and coating, which is detectable only by changing the color (the darker: surface and transparent: coating). This is one piece of evidence for the considerable mechanical strength endurance after 650-hour exposure to accelerated environmental conditions.

Cross-sectional view of the SEM image for the nitric acid treated PP-EPDM sample under conditions similar to those of the other samples is also shown in Figure 10. Obviously, the bond between the coating and the HNO_3 -treated surface is highly invulnerable so that, even at the highest magnification, no groove or hole can be diagnosed. These observations revealed that by electrochemical treatment, a higher degree of interfacial interaction formed between the primer and the treated surface, leading to mechanical interlocking as a driving force for improved adhesion strength [17]. In fact, the adhesion strength on the electrochemically-treated samples did not decline by aging, indicating that these samples had a quite stable surface. Since polar surfaces have inherently



Figure 9. Cross-sectional view of the SEM micrographs (magnifications $700 \times$ and $20000 \times$) for the acrylic-urethane coating on the Ag(II) treated sample after 650 hours of exposure to UV accelerated conditions (surface thickness: 34.81 μ m).



Figure 10. Cross-sectional view of SEM micrographs (magnifications $700 \times$ and $20000 \times$) for acrylic-urethane coating on the nitric acid treated sample after 650 hours of exposure to the accelerated conditions (surface thickness: 34.81 μ m).

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hydrophilic nature, water molecules can easily penetrate into the interface and disturb the adhesion between the treated surface and the paint.

Besides, after applying electrochemical treatment, especially by Ag (II), the chance for gas diffusion by gases such as O_2 , nitrogen, and SO_2 as well as moisture diffusion from surface to depth is minimized. As a result, there is a remote possibility for creating chromophores as the main cause of discoloration.

There is a good correlation between the result of cross-sectional view of the SEM image and UV accelerated analysis performed according to ASTM D4587-11, as shown in Figure 6(a)-(d), because increase in the yellowing of the polyurethane surface is due to the presence of groove or hole at the interface of the substrate and base coat. On the other hand, the higher the separation at the junction coating to the surface, the higher the chance for gas diffusion from surface to depth, which leads to color change during the exposure to UV irradiation.

These results fully comply with those obtained for adhesion strength of coating on the same treated samples, as evident in Figure 11. According to Figure 11(a), the trend of coating adhesion failure after electrochemical treatments by Ag (II) is rather different from that of the flame treatment method.



Figure 11. The pull-off adhesion test: (a) Adhesion strength vs. extension and (b) bar chart with standard deviation for different treated blends.



Figure 12. Zeta potential analysis of different treated PP-EPDM blends.

The fracture of the films in Ag (II)-treated samples occurs at higher extensions and forces than that in the flame-treated sample. Figure 11(b) solely compares the maximum adhesion strength for these samples. As observed earlier, the highest adhesion strength of the acrylic-urethane coating onto the PP-EPDM sample corresponds to the Ag (II)-treated sample, which has been enhanced ten times more than the untreated PP-EPDM sample.

Zeta potential measurement was performed to determine the isoelectric point (IEP) and surface charge properties such as functional sites. The variations in zeta potential with pH for the untreated and electrochemically treated samples are depicted in Figure 12. As is clear, the ζ -pH plot of the untreated PP-EPDM surface is a curve with no plateau, which is a typical characteristic of a non-polar surface due to the lack of functional groups. However, after performing flame treatment, S-shaped curves were attained and their IEPs shifted to higher pH values. Flame treatment also changed the acidity and basicity of the surface. In the case of the Ag (II)-treated sample, a shift of IEP to a lower pH is detected as compared to the untreated sample. This is a typical graph for acidic surfaces because of the curve IEP shifting to lower pH values. Moreover, in this case, increase in negative zeta potential with a specific pH may result from the adsorption of OH⁻ ion on the surface as well as dissociation of acidic groups.

4. Conclusions

The effect of electrochemical treatment on the adhesion of acrylic-urethane paint onto a PP-EPDM bumper was investigated in the long term by ATR, SEM, and accelerated UV weathering analysis along with SEM study. Aging of the Ag (II) treated PP-EPDM sample did not lead to a significant change in the surface properties. Accelerated UV weathering analysis confirmed the effectiveness of the Ag (II) treatment in the long term, particularly at curvature and lowaccess area of the bumper. Accelerated UV analysis revealed that, after exposure to wet conditions, unlike the untreated and flame-treated PP-EPDM samples, the adhesion strengths for the Ag (II)-treated sample remained almost intact. In fact, the aging of Ag (II)-treated surface after three months did not lead to significant surface changes. In the case of flametreated surface, however, hydrophobic recovery during aging in the environment reduced the polarity of the PP-EPDM surface layer. Finally, MEO by Ag (II) considerably improved surface adhesion strength of the acrylic-urethane coating onto the PP-EPDM compared to the conventional flame-treatment by 20.7%. Zeta potential measurements for Ag (II) treated blends also proved acidic surface of functional surface sites.

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