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Improved Adhesion of UV Treated EVA Copolymer by Adding Small Amounts of Fillers

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

Adhesion and Adhesives Laboratory, Department of Inorganic Chemistry, University of Alicante, 03080 Alicante, Spain
E-mail: md.landete@ua.es

Summary: The influence of adding small amounts of calcium carbonate or sepiolite fillers on the adhesion properties of UV surface-treated ethylene vinyl acetate copolymer (EVA) was studied. In this paper, it has been demonstrated that the addition of 3-7 wt% filler enhanced the extent of the surface modifications (wettability, surface chemistry, roughness) and increased the adhesion of EVA. These effects were more marked when 7 wt% sepiolite filler was added to EVA, likely due to its higher aspect ratio.

Keywords: EVA; fillers; infrared spectroscopy; peel strength; UV treatment

Introduction

Ethylene vinyl acetate (EVA) copolymers are commonly used as sole materials in the footwear and toy industries due to their chemical resistance, light weight, flexibility and toughness. However, adhesion of EVA is poor due to its low surface energy, and, therefore, a surface treatment is necessary. Several treatments (corona discharge, low-pressure oxygen or air plasmas) resulted in the formation of polar moieties and increased surface energy, which led to enhanced adhesion of different polymers [1], including polyolefins. On the other hand, the UV-ozone treatment has been used to increase the wettability of poly(ethylene terephtalate) (PET), polyethylene (PE), and polypropylene (PP) [2,3]. Furthermore, it has been shown [4] that the UV radiation treatment improved the wettability and adhesion of unfilled EVA-polyethylene foams and injection moulded EVA [5].

On the other hand, polyolefins are usually loaded with fillers (calcium carbonate, silica, silicates) to increase their mechanical properties and/or to reduce costs. The way in which the fillers affect the effectiveness of the surface modifications and adhesion of polyolefins has not been already considered in the existing literature. In this study, the surface modifications and adhesion of an EVA filled with small amounts of calcium carbonate or sepiolite were considered.

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Calcium carbonate is the most widely used filler for plastics, paper, paints and coatings (milled grades), and it is also employed in emulsion paints, printing inks, cigarette paper, pharmaceutical preparations, and toothpaste (precipitated grades). As examples, the addition of calcium carbonate improves the impact strength and inhibits the migration of additives in PVC [6]. In PE and PP films, calcium carbonate filler acts as anticaking agent [7].

Sepiolite ($Si_{12}O_{30}Mg_8(H_2O)_4(OH)_4 \cdot 8H_2O$) is a hydrated magnesium aluminum silicate, with layered talc-like structure composed of ribbons with two sheets of tetrahedral silica units linked by means of oxygen atoms to a central octahedral sheet of magnesium cations. Sepiolite is less used as filler because its deposits are relatively rare in comparison with the other industrial clays, and Spain is the largest producer (it accounts for about 95% of the world's annual production) [8]. Sepiolite is used in several applications owing to its fibrous structure, relatively high aspect ratio and high porosity [9]. The major uses of sepiolite are in drilling muds, paints, liquid detergents, adhesives, car polishing, filler in plastics and rubber, blend compatibilizer, cosmetics and also as a binder for pelletized animal feed. PP filled with sepiolite shows improved bending and tensile strength [10]. Sepiolite was also used to improve the adhesion of solvent-based polyurethane adhesives [11,12].

Previous studies [13] showed that, after plasma treatment, similar degree of surface modification and adhesion improvement was obtained in filled EVA with 3 to 20 wt% $CaCO_3$. Optimum performance was obtained in EVA containing 3 wt% $CaCO_3$. On the other hand, it has been shown that the adhesion of EVA can be improved by addition of 3 to10 wt% of sepiolite [14], showing a slight increase in adhesion by increasing the amount of sepiolite. However, the addition of 10 wt% sepiolite imparted stiffness to EVA, so a loading of 7 wt% was considered as optimum.

Therefore, in this study small amounts of calcium carbonate (3 wt%) and sepiolite (7 wt%) were used as inert and reinforcement fillers for one EVA copolymer containing 12 wt% vinyl acetate – EVA12. The surface modifications produced by UV-ozone treatment and the adhesion properties of unfilled and filled EVA12 were compared.

Experimental

The EVA12 pellets were supplied by Repsol Química, S.A. (Santander, Spain). This material has a melt flow index of 0.6 g/10 min and a Shore D hardness of 40 [15].

EVA12 was mixed with 3 wt% $CaCO_3$ – EVA12C - or 7 wt% sepiolite – EVA12S - in a extruder. The unfilled and filled EVAs were moulded using a Margarit JSW injection machine to obtain test samples of 150 x 60 x 2 mm^3. These samples were cut into 150 x 30 x 2 mm^3 for adhesion tests.

Sepiolite was supplied by Tolsa, S.A. (Madrid, Spain). This filler contains needle shaped particles (2 µm length, 50-100 Å thick). The natural micronized calcium carbonate was supplied by S.A. REVERTÉ (Tarragona, Spain) and has a mean particle size of 1.9 µm. Some properties of the fillers are given in Table 1.

Table 1. Some properties of sepiolite and calcium carbonate [16] .

Property	$CaCO_3$	Sepiolite
Density (g/l)	400 (uncompacted) – 700 (compacted)	60
Moisture content (wt%)	<0.1	8
Melting point (°C)	—	1550
pH	8.8	8.7
DOP (dioctyl phthalate) absorption (g DOP/100g)*	27	250
BET surface area (N_2/77K) (m^2/g)	14.5	270

*ISO 787-5 standard.

Adhesion of UV-treated EVAs were obtained from joints made with a two-component solvent-based polyurethane adhesive based on Desmocoll 540 pellets supplied by Bayer AG (Leverkusen, Germany). This polyurethane has a high crystallization rate and a short open time. Adhesive solutions were prepared by dissolving 18 wt% solid Desmocoll 540 pellets in butanone in a laboratory mixer using a Cowles stirrer (3 h, 850 rpm, 25°C). 5 wt% Desmodur RFE polyisocyanate (Bayer AG, Leverkusen, Germany) was added immediately before adhesive application.

The UV radiation source was a low-pressure vapour grid mercury lamp, manufactured by American Ultraviolet (USA). The lamp works at the wavelength of 254 nm, which provided a radiation intensity of 10 mW/cm^2 taken at a distance of 2.54 cm from the lamp. Samples were treated on a platform mounted 2.0 cm under the UV lamp. The length of the treatment was varied between 1 and 5 minutes.

The changes in the surface properties of EVAs due to UV radiation treatment were measured using different experimental techniques.

Contact angle measurements. They were carried out in a thermostated chamber (25 °C) of a Ramé Hart 100 goniometer. The chamber was previously saturated with the vapour of the test liquid at 25 °C (bidistilled and deionized water) for at least 10 minutes before placing a 4 μl drop of the test liquid on the EVA surfaces. Advancing contact angles of deionized and doubly distilled water were measured on just UV-treated EVAs. The experimental error was ±2 degrees.

ATR-IR spectroscopy. The use of attenuated total reflectance technique of IR (ATR-IR) examination allows a very thin surface layer (2 to 5 μm depth, depending on prism nature and experimental conditions) to be examine by clamping a specimen to a prism from which the IR radiation is reflected. The infra-red spectra of the treated samples were obtained in a Nicolet FTIR 5DXB spectrometer provided with a thallium bromo-iodide crystal; the incident angle was 45° and 200 scans were collected and averaged at a resolution of 4 cm^{-1}. Under the experimental conditions used in this study, the ATR-IR spectroscopy allows to analyze about 2 μm of the treated EVA surface.

X-ray photoelectron spectroscopy (XPS). A VG Scientific Microtech Multilab spectrometer with a MgK_{α} X-ray source (1253.6 eV) operating at 15 keV and 300 W was used; a 45° incidence angle was used. The analysis was performed on 5 x 2 mm pieces of EVA at a residual pressure below 10^{-8} Torr. For each sample, a survey scan encompassing the region 0-1200 eV was first obtained. Multiplex scanning of all observed photopeaks in the survey scan were carried out in a 20 eV range. Binding energies of all photopeaks were referenced to the C 1s photopeak position for C-C and C-H (hydrocarbons) species at 285.0 eV. 1.8 eV was used as FWDH for the carbon peak.

Scanning electron microscopy (SEM). The morphological modifications produced on the treated EVA surfaces were analyzed using a *JEOL JSM-840 SEM* microscope. The samples were gold-coated and the energy of the electron beam was 20 kV.

T-peel strength. Adhesive joints using two similarly treated EVAs were produced. Immediately after UV treatment, about 0.8 ml of polyurethane adhesive solution was applied to each EVA test specimen using a brush. After allowing the solvent to evaporate for 20 min, the dried polyurethane adhesive films on the surface-treated EVA were melted for 10 seconds at 100°C using infrared radiation. These specimens were then placed in contact and a pressure of 0.8 MPa was applied for 10 s to achieve a suitable joint. The T-peel strength was measured using an Instron 4411 instrument (peel rate = 100 mm/min). The values obtained were the average of three experimental replicate determinations (standard deviation was less than 10%). The adhesive joints were kept at 25°C and 50% relative humidity before undergoing the T-peel test. Adhesion was measured 72 hours after joint formation.

Results and Discussion

The water advancing contact angle values on EVA surfaces (Figure 1) decrease by increasing the length of the UV treatment. Unfilled and filled EVA12 show similar trend but somewhat lower values were obtained in the UV treated filled EVAs. Therefore, the UV treatment increases the wettability of EVA12, more markedly when a small amount of filler is added, irrelevant of its nature.

The decrease in the contact angle values can be ascribed to modifications in the surface chemistry and/or morphology of EVAs.

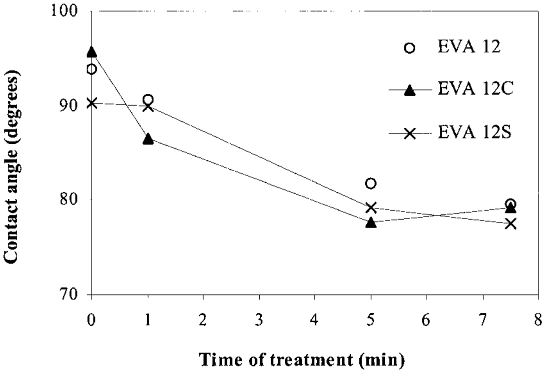

Figure 1. Water (25°C) advancing contact angles on EVAs treated with UV radiation.

Figure 2 shows the ATR-IR spectra of the as-received and UV treated EVAs. The ATR-IR spectra of the as-received EVAs show 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}. The filled EVAs also show the typical bands of the fillers : Bands at 880 and 1437 cm^{-1} due to the CO_3^{2-} group (EVA12C), and bands at 1017 and 480 cm^{-1} due to Si-O group (EVA 12S). The UV treatment decreases the relative intensity and increases the width of the C=O band at 1739 cm^{-1}, indicating the formation of new oxygen-containing moieties on the treated EVA surfaces. However, because of about 2 μm thick EVA is analyzed by ATR-IR spectroscopy, a more sensitive surface analysis technique was used to determine the surface modifications produced on the EVA surfaces by UV treatment.

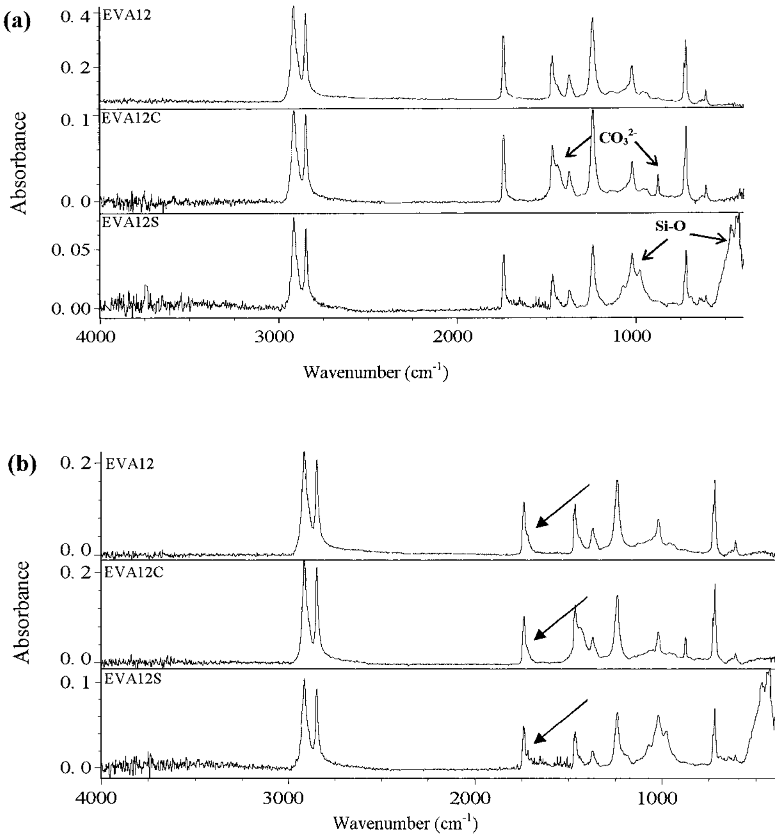

Figure 2. ATR-IR spectra of the (a) as-received and (b) UV-treated (5 min) EVAs.

Table 2 shows the elemental composition on the as-received and UV-treated EVAs obtained using XPS. As-received EVA12 is mainly composed of carbon and a small amount of oxygen. EVA12S contains small amounts of Si and Mg due to the presence of sepiolite particles on the surface, but Ca is not present on the surface of EVA12C. Because XPS analyses about 5 nm surface and Ca is shown in the ATR-IR spectra of the as-received EVA12C (about 2 μm depth is analyzed), the $CaCO_3$ particles on the surface must be covered by a thin layer of polymer.

Table 2. Elemental composition on the as-received and UV-treated (5 min) EVA surfaces. XPS experiments.

Sample	Element	As-received	UV treated	
			1 min	5 min
EVA 12	C	95.2	95.2	92.8
	O	4.8	4.8	7.2
	O/C	**0.05**	**0.05**	**0.08**
EVA 12C	C	95.2	95.0	92.1
	O	4.8	5.0	7.9
	Ca	---	---	---
	O/C	**0.05**	**0.05**	**0.09**
EVA 12S	C	91.0	85.8	81.7
	O	7.1	10.4	14.2
	Si	1.8	3.7	3.9
	Mg	0.1	0.1	0.2
	O/C	**0.08**	**0.12**	**0.17**

The UV treatment for 5 min produces an increase in oxygen and consequently in the O/C ratio on the treated EVA surfaces. For a shorter UV treatment an increase in oxygen content is only found on the EVA12S surface. Furthermore, the extent of the surface modifications are more marked in the filled EVA12, mainly when sepiolite is added, indicating an effect of the filler content and nature in the modifications produced on the EVA surface by treatment with UV radiation.

Figure 3 shows the percentages of carbon species obtained from C1s curve fitting of as-received and 5 min UV-treated EVAs. As-received EVAs show the typical bands corresponding to EVA: 285.0 eV (C-C, C-H), 285.6 eV (C^*H_3-(C=O)-O), 286.6 eV (HC^*-O-(C=O)-), and 289.2 eV ((C^*=O)-O). The UV treatment decreases the amount of C-C and C-H species (285.0 eV), an slight increase in C-O moieties is produced, and new C=O moieties (288.0 eV) are created. The presence of calcium carbonate or sepiolite produces a more noticeable decrease in C-H moieties on UV-treated EVA12C and EVA12S, and a more marked increase in C-O groups in EVA12S.

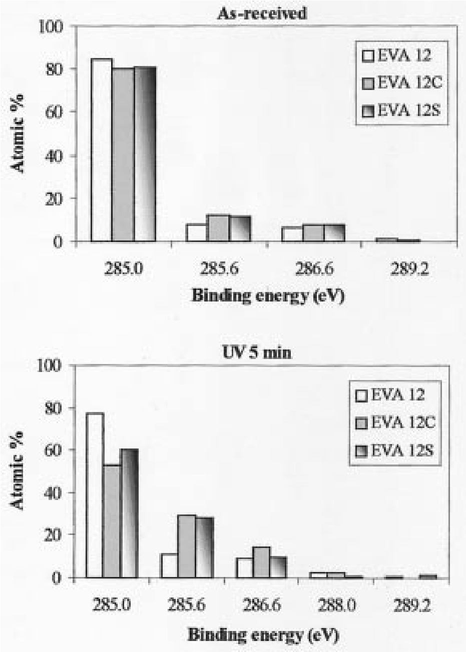

Figure 3. Distribution of C1s species on (a) as-received and (b) UV treated (5 min) EVA surfaces. XPS experiments.

The UV treatment also modifies the morphology of EVAs. SEM micrographs (Figure 4) show some cracks on the surface of treated EVA12. As-received filled EVAs (EVA12C and EVA12S) show a more heterogeneous surface (small particles of $CaCO_3$ and sepiolite appear on the surface) than the unfilled EVA12, and the UV treatment generates more degraded surfaces in a non-uniform way.

As a consequence of the chemical and morphological modifications on the EVAs produced by UV-treatment, improved adhesion in EVA 12/polyurethane + 5 wt% polyisocyanate adhesive joints is produced (Figure 5).

The joints produced with the as-received EVA12 show very low peel strength values due to the poor wettability and the non-polar nature of the copolymer, irrelevant to the presence or not of fillers. However, the UV treatment of EVAs increases the peel strength values, which is in agreement with the improvement in wettability, and the creation of roughness and surface chemistry. The UV treated sepiolite filled EVA12 show the highest adhesion improvement, in agreement with the greater extent of the surface modifications produced by the treatment.

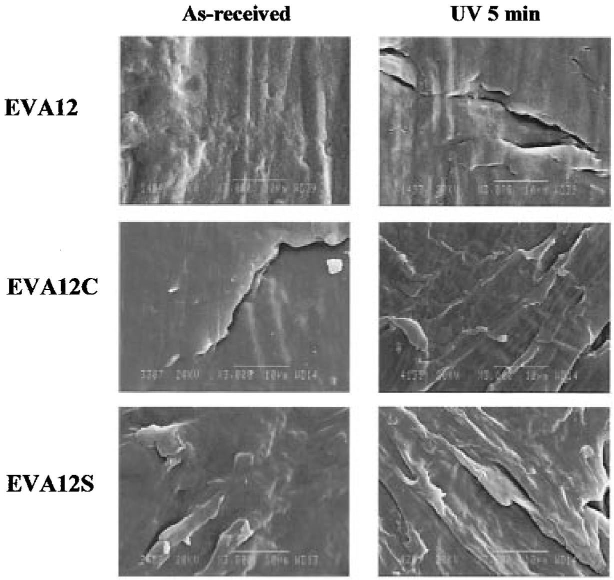

Figure 4. SEM micrographs of as-received and UV treated (5 min) EVAs.

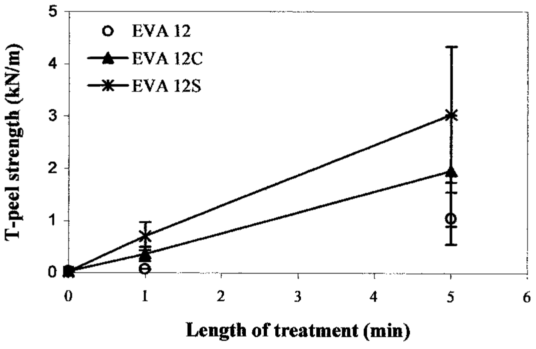

Figure 5. T-peel strength of as-received and UV treated EVA 12/polyurethane + 5 wt% polyisocyanate adhesive joints.

Conclusions

The UV treatment increases the adhesion of EVAs to polyurethane adhesive due to improved wettability, and the creation of roughness and C-O and C=O moieties. The presence of small amounts of $CaCO_3$ or sepiolite fillers in EVA 12 enhanced the extent of the surface modifications, and better performance was obtained when 7 wt% sepiolite is used as filler for EVA12.

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