# Influence of the Particle Size of $CaCO_3$ on the Adhesion of Filled EVA Materials

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**Summary:** A surface treatment with corona discharge was used to improve the adhesion properties of ethylene vinyl acetate copolymer (EVA) containing small amounts of four $CaCO_3$ with different particle size. The nature of the surface modifications produced by the corona discharge treatment and the adhesion to a polychloroprene adhesive were assessed. Treatment of $CaCO_3$ filled EVA with corona discharge produced a decrease in water contact angle value, irrelevant to the different particle size of the calcium carbonates. The corona discharge treatment created C-O and C=O moieties on the EVA surface and also increased the peel strength, more markedly as the $CaCO_3$ particle size increased. In general, a mixed (adhesion + cohesive in the EVA) failure in the filled EVA material was produced (assessed by IR-ATR spectroscopy and SEM micrographs of the failed surfaces), but the failure was more cohesive in the EVA containing higher particle size $CaCO_3$. The durability of the joints was also studied.

**Keywords:** adhesion; $CaCO_3$; corona discharge; EVA; IR spectroscopy; T-peel strength

## Introduction

The particle size of the fillers usually determines the filler-polymer interactions and the mechanical properties of polymers [1]. In general, the smaller the filler particle size, the better the mechanical properties, but the viscosity is poorer and the mixture is more difficult to process [2], due to the agglomeration of primary particles. As the particle size of $CaCO_3$ increases, its specific surface area decreases. Adhesion performance of polymers is also affected by the filler nature and particle size. Therefore, in this study, corona discharge was used as a surface treatment to improve the adhesion properties of two EVA copolymers containing four $CaCO_3$ with different particle size. Corona discharge is a fast treatment, it can be easily adapted to industrial production, and it produces an increase in the adhesion of several polyolefins [3-5].

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## Experimental

The EVA12 pellets were supplied by Repsol Química, S.A. (Santander, Spain). The melt flow index of EVA12 is 0.6 g/10 min and its Shore A and D hardnesses are 96 and 45, respectively. Unfilled and filled EVA12 were moulded using a Margarit JSW injection machine, and the following conditions were used : Temperature = 170 °C; injection time = 6 s; injection pressure = 60 % of total pressure (1570 bar; 1 bar=$10^5$ Pa); mould temperature = 20 °C. The copolymer was filled during the injection process with 5 wt% of four ultramicronized and calcium stearate surface treated $CaCO_3$ fillers (supplied by S.A. Reverté, Bellvei, Spain). The four $CaCO_3$ have different mean particle sizes (0.6, 1.0, 1.8 and 4.0 μm) and different specific surface areas ( 14.5, 11, 6 and 3 $m^2/g$, respectively), and in this study they are referenced as T1, T2, T3 and T4, respectively. The injection moulded pieces were cut into test samples of sizes 20×30×2 mm for characterization and 150×30×2 mm for adhesion tests.

Adhesive joints of treated $CaCO_3$ filled EVA12 were made using a commercial two-component solvent-based polychloroprene adhesive consisting of polychloroprene adhesive itself (Telcopren 3003, supplied by Composan Adhesivos S.A., San Vicente del Raspeig, Spain) and 5 wt% polyisocyanate (Desmodur RF, provided by Bayer, Leverkusen, Germany). The adhesive and the isocyanate were mixed just before application using a brush on two identically treated filled EVA12 strips. The adhesive was cured in open air for 1 hour and afterwards melted at 100°C by using an infrared lamp (to facilitate the interlocking of the chains of the adhesive). The two strips were then placed in contact and a pressure of 0.8 mPa was applied for 10 seconds to achieve a suitable joint. The polychloroprene adhesive solution contains 25 wt% solids and its Brookfield viscosity is 3.0 ± 0.2 Pa.s. The thickness of the adhesive layer applied on EVA12 was about 100 μm.

A Tantec Corona Generator model HV09 was used to modify the unfilled and $CaCO_3$ filled EVA. The distance between the upper electrode and the sample was adjusted to 1 mm. The sample was located on the counterpart nylon electrode, which could be displaced at a controlled speed. A hook-shaped electrode was used, and the treatment was performed in air at atmospheric pressure. The discharge power was set to 93 W and 150 mm long EVA samples were passed under the electrode at a speed of the counterpart nylon electrode of 19 mm/s. These conditions provide a corona energy of 3.3 $J/cm^2$. The corona energy was obtained using the following equation:

$$\text{Corona energy} = \frac{\text{Power}}{\text{Speed x treatment length.}}$$

Contact angle values on the treated $CaCO_3$ filled EVA12 were measured at 25 °C using a Ramé-Hart 100-0 equipment by placing 4 μl drops of deionized and doubly distilled water on the surface. The samples were placed into a chamber saturated with water vapour at 25 °C, at least 15 min before the drop was placed on the filled EVA12 surface. The contact angle values were measured immediately after corona discharge treatment. The experimental error was ± 2 degrees.

ATR-IR spectra of corona discharge-treated $CaCO_3$ filled EVA12, before and after T-peel tests, were obtained using a Nicolet FTIR 550 spectrometer. To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed using a KRS-5 (thallium bromo-iodide) crystal. The incident angle of the IR radiation was 45°. 100 scans were averaged at a resolution of 4 $cm^{-1}$.

SEM micrographs of the as-received and corona discharge treated unfilled and $CaCO_3$ filled EVA12, before and after T-peel tests, were obtained in a JEOL SEM J840 instrument using an electron beam energy of 20 kV. The samples were gold coated and the electron beam was 20 kV.

The adhesion was evaluated from T-peel tests on as-received and treated $CaCO_3$ filled EVA12/polychloroprene adhesive joints (72 hours after bond formation) using an Instron 4011 instrument; a crosshead speed of 0.1 m/min was used. Five replicates for each experimental variable were obtained and data were averaged with an error less than ± 0.5 kN/m.

## Results and Discussion

Figure 1 shows the SEM photographs of the four $CaCO_3$ where the shape and the different degree of agregation of the particles can be appreciate. As the $CaCO_3$ particle size decreases, the degree of agregation is higher.

The ATR-IR spectra of the 5 wt% $CaCO_3$ filled EVA12 (Figure 2) correspond to that of the EVA12 and also typical bands of the calcium carbonate at 1437 and 874 $cm^{-1}$ appear, indicating that a physical mixture of the components was obtained.

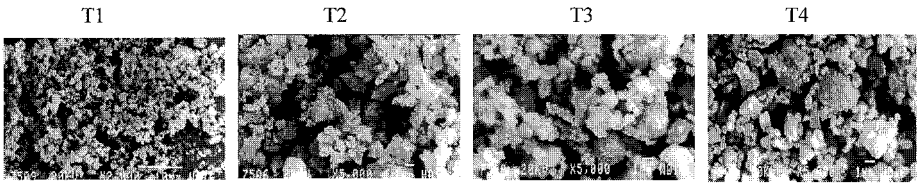


Figure 1. SEM micrographs of the $CaCO_3$ fillers.

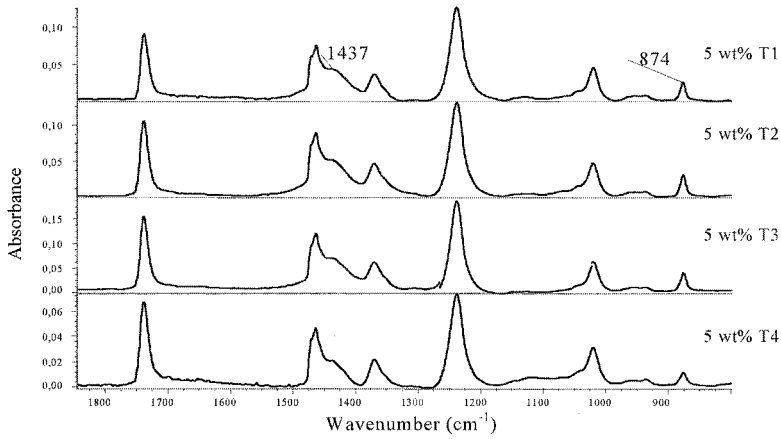


Figure 2. ATR-IR spectra of the different particle size $CaCO_3$ filled EVA12.

The corona discharge treatment of the different size $CaCO_3$ filled EVA12 was carried out at a corona energy of 3.3 J/cm$^2$. The contact angle values of filled EVA12 (Figure 3) decrease from 89-94 degrees (untreated) to 53-48 degrees (after corona discharge treatment), and these values are similar for all EVA12 containing $CaCO_3$ of different size.

The ATR-IR spectra of the corona discharge-treated T1, T2 and T3 $CaCO_3$ filled EVA12 show that the carbonate bands at 1437 and 874 cm$^{-1}$ are more intense than that of the untreated material, indicating that the treatment exposes $CaCO_3$ particles to the surface. The ratio of the relative intensities at 874 cm$^{-1}$ (typical of $CaCO_3$) and 1238 cm$^{-1}$ (typical of EVA12) bands increases after corona discharge treatment (Table 1); that is, some EVA is removed by treatment with corona discharge and some $CaCO_3$ particles become exposed to the surface.

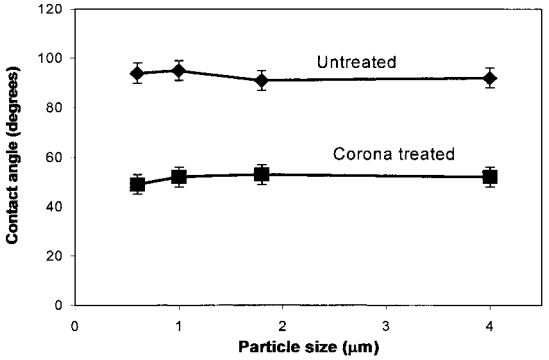


Figure 3. Contact angle values (water, 25°C) on EVA12 filled with 5 wt% $CaCO_3$ of different particle size.

Table 1. Ratio of the relative intensities at 874 $cm^{-1}$ ($CaCO_3$) and 1238 $cm^{-1}$ (EVA12) bands (ATR-IR spectra) in the EVA12 filled with 5 wt% $CaCO_3$ of different particle size.

| Material | Untreated | Corona discharge-treated |
|---|---|---|
| EVA-T1 | 0.21 | 0.50 |
| EVA-T2 | 0.24 | 0.44 |
| EVA-T3 | 0.24 | 0.46 |
| EVA-T4 | 0.15 | 0.17 |

The ratio of the relative intensities in the corona discharge-treated T4 filled EVA12 is similar to that of the untreated material, which could indicate that the filler particle size affects the interaction of $CaCO_3$ with EVA12 and also the extent of the modifications produced by the corona discharge treatment. By increasing the particle size of the $CaCO_3$ a lower number of primary particles tend to agglomerate and this will allow a more homogeneous mixture with EVA12 during processing, in agreement with previous studies [6].

On the other hand, bands at 1460-1500 $cm^{-1}$ and 1640 $cm^{-1}$ appear in all ATR-IR spectra of the corona-discharge treated materials (Figure 4) indicating the formation of carbon-oxygen moieties (mainly C-O and C=O) [5].

As a consequence of the chemical and morphological modifications produced by corona discharge treatment, improved adhesion of $CaCO_3$ filled EVA12 is achieved (Table 2). Similar adhesion was obtained in the untreated materials filled with T2, T3 and T4 (0.7 kN/m). These

values increase after corona discharge treatment, more markedly for the joint produced with the EVA filled with the higher particle size $CaCO_3$ (T4).

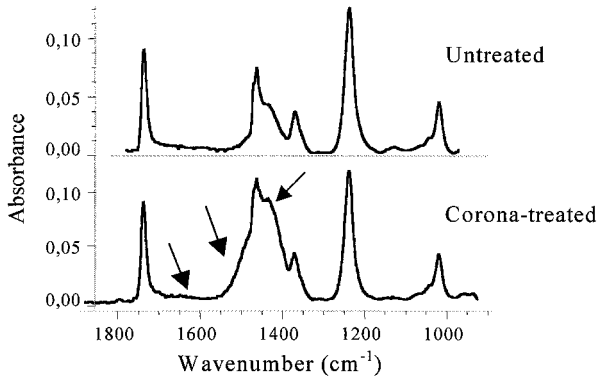


Figure 4. ATR-IR spectra of treated 5 wt% $CaCO_3$ filled EVA12 (T3).

Table 2. T-peel strength values (kN/m) of $CaCO_3$ filled EVA12/polychloroprene adhesive joints. Ageing conditions: 50°C/95 % relative humidity/72 hours.

| **Condition** | **EVA-T1** | **EVA-T2** | **EVA-T3** | **EVA-T4** |
|---|---|---|---|---|
| Untreated | 0.3 | 0.7 | 0.7 | 0.7 |
| Corona discharge-treated | 1.4 | 2.0 | 1.7 | 2.5 |
| Untreated+aged | 0.4 | 0.4 | 0.4 | 0.5 |
| Corona discharge-treated + aged | 2.4 | 3.2 | 2.1 | 3.1 |

In order to more precisely assess the loci of failure of the joints, the failed surfaces obtained after peel tests were analyzed using ATR-IR spectroscopy and SEM. The ATR-IR spectra of the failed surfaces show an adhesion failure in the untreated $CaCO_3$ filled EVA12 (Figure 5). The ATR-IR spectrum of one of the surfaces corresponds to the adhesive (A surface) and the other to the filled EVA12 (P surface). After corona discharge treatment the locus of failure of the joints changes. A mixed failure (adhesion + cohesion in EVA) is obtained, because some bands of filled EVA (C-O and C=O bands at 1238 and 1739 $cm^{-1}$; $CH_2$ and $CH_3$ bands at 2847, 2915 and 1464 $cm^{-1}$) can be distinguished in the ATR-IR spectrum of the A surface. This locus of failure is similar in all

joints but becomes more cohesive in the T4 filled EVA material (containing the $CaCO_3$ with higher particle size).

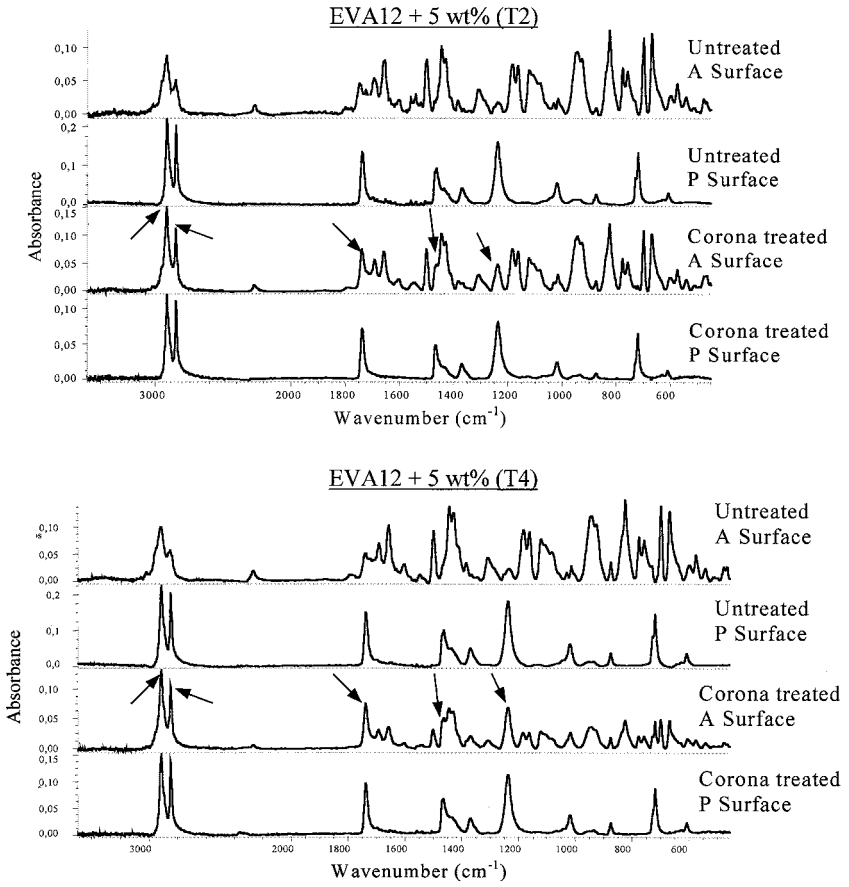


Figure 5. ATR-IR spectra of the failed surfaces obtained after peel tests of the joints produced with T2 and T4 filled EVA12.

The SEM micrographs of the failed surfaces of the $CaCO_3$ filled EVA/polychloroprene adhesive joints (Figure 6.a) show more ripped surfaces when treated with corona discharge, irrelevant to the particle size of the filler. All the SEM micrographs of the A surfaces show $CaCO_3$ particles

which are transferred from the P surface during peel test (Figure 6.b), the transfer is more important in the EVA12 filled with higher particle size calcium carbonate, T4. The SEM micrographs of the P surfaces of the corona discharge treated samples show some EVA filaments after the peel test, as a consequence of the higher strength required to peel out the joint.

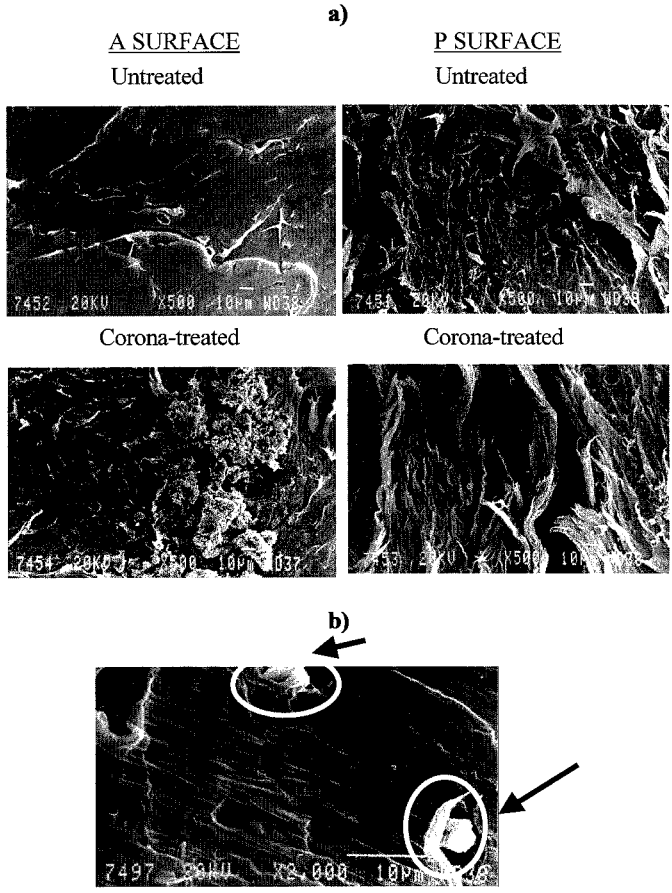


Figure 6. a) SEM micrographs of the failed surfaces obtained after peel test of the joint produced with T4 $CaCO_3$ filled EVA12; b) SEM micrograph of a zoomed part of the failed A surface.

Durability of the adhesive joints was studied by accelerated ageing tests. Table 2 shows that the ageing at 50°C and 95 % relative humidity for 72 hours produces an increase in peel strength

values in the adhesive joints produced with the corona discharge-treated filled EVA12. The peel strength values are higher for joints produced with T2 and T4 $CaCO_3$ filled EVA12 treated with corona discharge.

An adhesion failure of the aged untreated filled EVA12/polychloroprene adhesive joints was obtained, as shown by the ATR-IR spectra of the failed surfaces (Figure 7), but a cohesive failure is obtained for all the aged corona discharge-treated joints, independently of the particle size of the filler. This may likely indicates that the reaction of the polychloroprene with the polyisocyanate is completed during ageing, allowing an increase in the cohesive strength of the adhesive and thus a greater peel strength value is obtained.

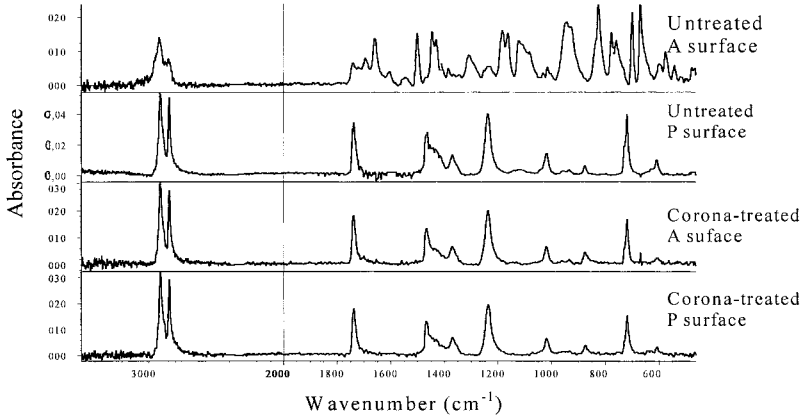


Figure 7. ATR-IR spectra of the failed surfaces obtained after peel tests of the aged adhesive joint of T4 $CaCO_3$ filled EVA12.

## Conclusions

The corona discharge treatment exposed $CaCO_3$ particles to the surface of EVA12, and it seemed that the dispersion of the filler was better with T4 carbonate (higher particle size). The corona discharge treatment increased the peel strength values and higher values were obtained for the EVA containing $CaCO_3$ with higher particle size (4 μm). In general, a mixed (adhesion + cohesion in EVA) failure in the corona discharge-treated materials was produced, but the failure

was more cohesive in the joint of T4 filled EVA12. The ageing of the joints increases the adhesion of the corona discharge treated materials.

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