# Influence of Corona Treatment on Adhesion and Mechanical Properties in Metal/Polymer/Metal Systems

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**ABSTRACT:** The effect of corona treatment (CT) on the adhesion at the metal–polymer interface was studied. Metal/polymer/metal laminates were manufactured by the laboratory roll-bonding process with preliminary corona surface treatment of the polymer core: a polyethylene and polypropylene sheet as well as steel sheet. It was treated with corona discharge to increase its surface energy and the adhesion to metal, an austenitic steel. The adhesion, which was measured by T-peel and shear tests, was increased by 43% of crack peel and 22% of mean peel resistance respectively, after 120 s CT. On the basis of scanning electron spectroscopy observations, improvements in the adhesive properties were attributed to the change in the interfacial morphology. In mechanical tests, yield and tensile strengths were strongly influenced by CT, indicating that these laminates were sensitive to interfacial phenomena. However, elongation at rupture of the composites was found to be unchanged. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3709–3715, 2011

**Key words:** metal/polymer/metal laminates; polyolefin; corona treatment; adhesion test; tension test

## INTRODUCTION

Metal/polymer/metal laminates (MPML) consist of alternating layers of metal and polymer, bonded by an adhesive layer.[1] These hybrid material systems have the potential to tailor the overall mechanical properties of the sandwich structure based on the properties of the constituents.[2] Because of their corrosion,[3] damping,[4] mechanical[5] and forming properties,[6] the low volume use of MPML and conventional composite materials have demonstrated success in aerospace[7] and automotive[8,9] applications. A good overview of their applications and the manufacturing techniques is given by Vinson.[2]

In many applications (e.g., in industry, technology), it is necessary to change and/or to improve some of the polymeric surface properties without modifying the bulk properties of the material.[10,11]

Therefore, it is necessary to gain a better understanding of the adhesive bonding properties between the metal and the polymer sheets, which can be modified by corona or plasma[12–14] discharge methods, of the surface treatment as well as the forming behavior of MPML, having different adhesive properties between the sandwich layers. Hitherto, not enough in-depth research has been carried out in this area.

Corona treatment (CT) is a method for increasing the surface energy to improve adhesion by means of activating the polymer and cleaning the metal[15] prior to joining the mating partners together by roll bonding. A corona discharge is an electrical process that uses ionized air to increase the surface tension of nonporous substrates. Normally, corona treating systems operate at an electrical voltage of some kilovolts. This one develops a current from an electrode with a high potential in air, by ionizing it to create plasma around the electrode. An overview about benefits of preliminary surface treatments and cleaning methods is given by Baldan.[12] The treatment improves the interaction of the surface with adhesives (e.g., epoxy resin) as well as the wettability of the surface without modifying the bulk properties.[16] As stated by different authors, an increased adhesion of corona-treated polymer surfaces is linked to:

- the elimination of weak boundary layers,[17]
- the surface roughness due to pitting[18] and
- the introduction of polar groups due to oxidation and other chemical changes in the surface region.[19–21]

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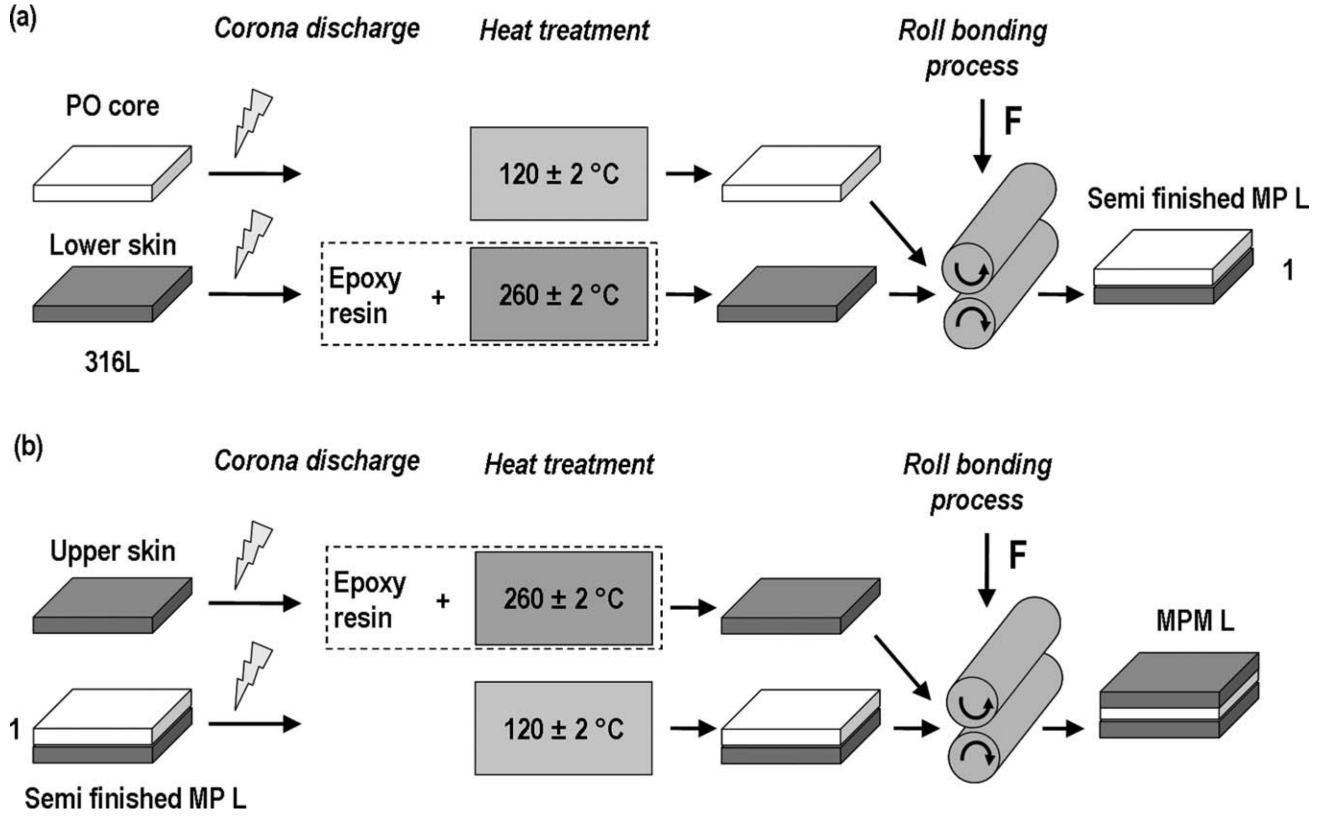

**Figure 1** (a) Production of roll-bonded metal-polymer and (b) production of MPML.

Some authors[22–26] have shown that the presence of polar groups and the morphology of the polyolefin films [PO, a mixture of polypropylene (PP) and polyethylene (PE)] play an important role in obtaining good adhesion. PO films have limitations to their adhesion properties due to their nonpolar nature and low surface tension. Zhang[16] showed the influence of CT on morphological, mechanical, thermal, and chemical surface conditions of PO films.

The effect of CT on the polymer can be explained as an anchoring of atoms or molecules coming from air onto the polymer surface.[27] The CT is used to introduce the reactive groups into a nonpolar polymer surface. A portion of radicals are stable in the polymer after exposure.

This process concentrates on the polymer surface at normal ambient atmospheric pressure and high voltage. The electric field's electrons are strongly accelerated as well as the oxygen and the nitrogen oxides. This ongoing process of ionization of the free electrons produces new molecules on the polymer surface. The process is linked to the contact surface energy of carbon–carbon (CC) or carbon–hydrogen (CH) bonds. Degradation of macromolecule's networking reactions and the formation of free macro radicals was observed.[16]

This paper focuses on corona discharge treatment of the PO core used for MPML. A laboratory roll bonding process was selected for the production of MPML systems. Effects of corona discharge treatment on the morphology were studied with a scanning electron microscope (SEM). The work of adhesion of MPML was evaluated by T-peel and shear tests; the mechanical properties were investigated using tensile tests.

## EXPERIMENTAL

### Processing of MPML systems

MPMLs are composed of 0.5 mm stainless steel (316L) cover sheets and a 0.6 mm polyolefin sheet core. Polyolefin consists of a mixture of PP and PE polymers as well as talc ($Mg_3Si_4O_{10}(OH)_2$), rutile ($TiO_2$), and barium sulphate ($BaSO_4$). Epoxy resin ®Kömmerling (Köratac FL 201) was used as an adhesive.

MPMLs were manufactured by laboratory roll-bonding (RB) process.[28–30] Before bonding, the metal and polymer sheets had to be cleaned, Corona treated and then metal sheet was coated with commercial epoxy resin and activated at (260 ± 2) °C for 3 min in a stationary convection oven. PO sheets had previously been heated at (120 ± 2) °C for 3 min. The first metal sheet was then joined to the PO sheet using a 10″ 2-high rolling mill [Fig. 1(a)]. In the next step, the semifinished sandwich product was bonded to the second metal sheet using the same procedure [Fig. 1(b)].

### Corona treatment

To improve the wettability and the porosity of the surfaces, corona discharge at atmospheric pressure was carried out before the RB process treating the polymer and the metal sheets with a corona device (®Tantec A/S, Denmark) for different times. Usually, there are two kinds of corona treating systems—with air gap and without air gap between the corona electrode and the sample (using contact of corona's roll with the surface of the sample). The air gap in the first corona system can be varied from 1 mm until level of centimeters.[31,32] The used corona system used a roll directly contacting the sample.

The system consists of a power supply,[33] a high voltage generator, a high frequency generator (typically 200 W, 13 kV, and 20 kHz), a control box, and a corona station. Ozone gas was created by applying a high potential between two electrodes: the roll and the sheet being in contact. PO films were treated for 20, 60, and 120 s.

### Thermal and morphological characterisation

The thermal decomposition was studied by means of Differential Scanning Calorimetric analysis (DSC) and Thermo Gravimetric Analysis (TGA). DSC analyses were performed on a SDT Q600.

Morphological observations were performed using a field emission microscope JEOL JSM-6700F operating at 3 kV on PO foil gold coated sheets prior and subsequent to CT.

### Adhesion tests

The adhesion between the polymer core and metal sheets was investigated on a universal materials testing machine using T (180°) peel tests, according to DIN 53282.[34] The dimensions of the MPML specimens were 170 mm × 30 mm × 1.5 mm. Six samples were used and the results were averaged for each data point.[35]

The adhesive and bond strengths between the metal and the polymers are key factors for MPML and the T-peel test is the most convenient method of comparing such interfaces. Peel tests do not provide absolute material data. The angle peel test according to DIN 53282 serves to determine the resistance of metal/polymer/metal bonds to peeling forces. The test is primarily used for the comparative assessment of adhesives and adhesive bonds. Peeling load (crack force, $F_A$) and initial crack strength (peel resistance, $P_A$) are defined as $F_A$ [N] and $P_A = \frac{F_A}{b}$ [N/mm], respectively, where b is the width of the test sample, here: 30 mm. Adhesion strength ($\overline{F}$) and mean peel resistance ($P_s$) are defined as $P_s$ [N] and $P_S = \frac{\overline{F}}{b}$ [N/mm] respectively, where b is the width of the sandwich sample (30 mm). The relation between crack peel resistance and mean peel resistance depends on the mechanical properties, such as Young's modulus and shear modulus or yield strength (YS) as well as on the dimensions and preparing method of the specimens.

The shear tests were carried out using a universal materials testing machine, according to QVA-Z10-46-09 (Daimler Benz Aerospace Airbus tests).[36] The 200 mm × 30 mm × 1.6 mm metal-polymer-metal sandwiches have opposing notches. The shear area was 360 $\text{mm}^2$ and the cutting width was 2.5 mm.

The shear strength (P) is defined as the maximum load ($F_{\max}$) divided by the shear area (A) $P = \frac{F_{\max}}{A}$ [$\text{N/mm}^2$]. Four samples were used for each type of sandwich material. The results were averaged for each data point.

### Mechanical tests

To measure the YS, tensile strength (TS), and rupture elongation (ER) of MPML, tensile tests were carried out on a universal testing machine (according to DIN EN 10002[37]) with an initial strain rate of $1.67 \times 10^{-3}\ \text{s}^{-1}$. For this purpose, tensile specimens with a gage length of 120 mm were prepared from 316L/PO/316L sandwich sheets prior and subsequent to their PO core CT for 120 s. "L" characterises the roll-bonded MPML parallel to rolling direction (RD) of the metal sheet. In addition, "T" represents the MPML, which has been produced turning the second metal sheet with its RD perpendicular to the RD of the first one. This is schematically depicted in Figure 2.

To determine the anisotropic behavior, the tensile tests were performed on "L" and "T" specimens taken at $\alpha = 0°$ and 90° to the roll bonding direction. To avoid delamination at the edges of the samples MPML, the samples were prepared by water-jet cutting.

## RESULTS AND DISCUSSION

The DSC curve of PO, as shown in Figure 3, has an exothermic melting peak with an onset at 147.6°C followed by a large exothermic peak with an onset at 251°C due to decomposition.

TGA shows (Fig. 4) a sharp decomposition, starting at 262°C. The weight loss at 500°C was 87%. Thirteen percent are due to the degradation of inorganic fillers such as talc, rutile and barium sulphate used by the industry. This test confirms that the choice of this PO was well adapted for the temperature range.

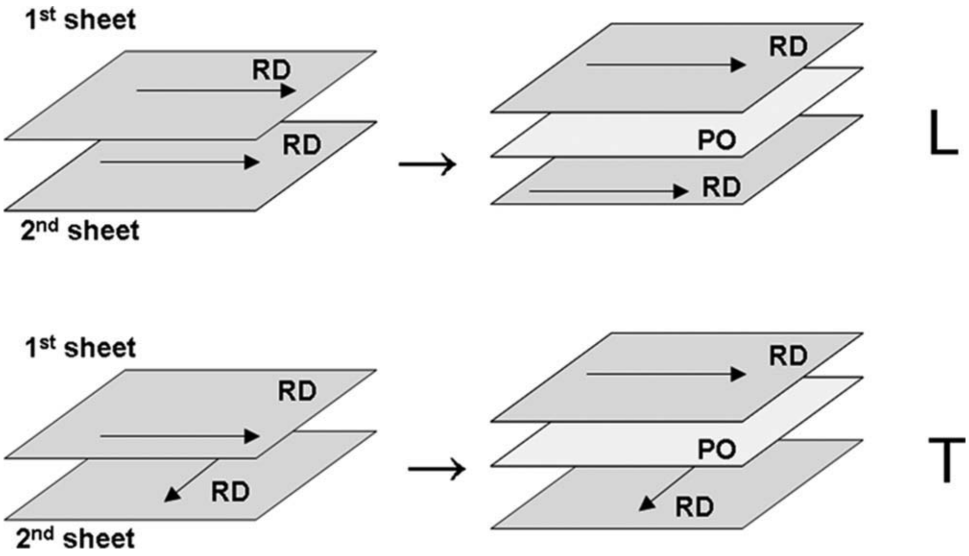

**Figure 2** Schematic of "T" and "L" MPML for the tensile tests.

The effect of CT on the morphology and roughness of the polymer and steel surfaces has been experimentally proven. The SEM images of the PO films show significant changes of the surface morphology induced by the CT (Fig. 5). Holes (pores) and an irregular porosity distribution can be detected, which are important for the adhesion properties as shown by Tsai et al.[38] Indeed, as energy particles bombard the PO sheet during treatment, small micro pits can be formed. These micro pits are microscopic holes excavated by the charges. Micro pitting can lead to increased adhesion due to a larger potential bond area. After corona discharge treatment, POs SEM images exhibit a large density of pores, an "etched character" with an irregular shaped structure and a bubble-like surface texture surrounding the pores, as can be seen in Figure 5(a,b).

Increasing corona time from 20 to 120 s no visible effects of morphology change could be observed for the steel surface (Fig. 6).

Investigation of wettability induced by CT was done only qualitatively using a contact fluid as described in.[39] The polyolefin used has a polarity near-zero, therefore a poor wettability, observed by low ink adhesion on the surface.

The bar chart in Fig. 6 shows a strong increase in crack-peel resistance (28%) and a mean peel resistance (43%) with increasing corona exposure time from 20 to 120 s. Moreover, an improvement of the shear resistance (22%) is measured following CT preparation. A linear tendency of improvement is observed in either Figure 7 or Figure 8.

These results can be explained by the creation of the polar chemical functional groups due to the

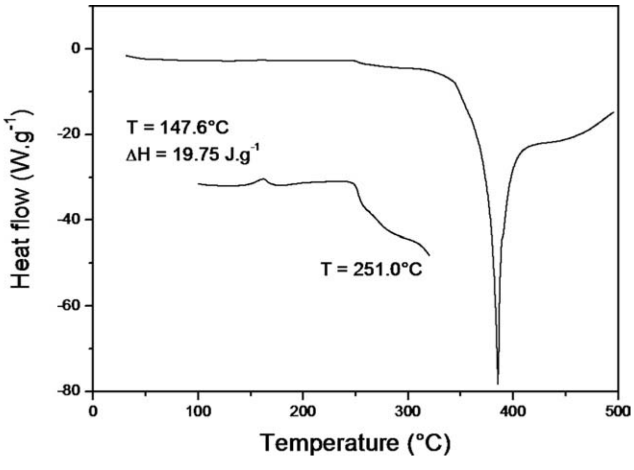

**Figure 3** DSC analysis of polymer core for sandwich structures.

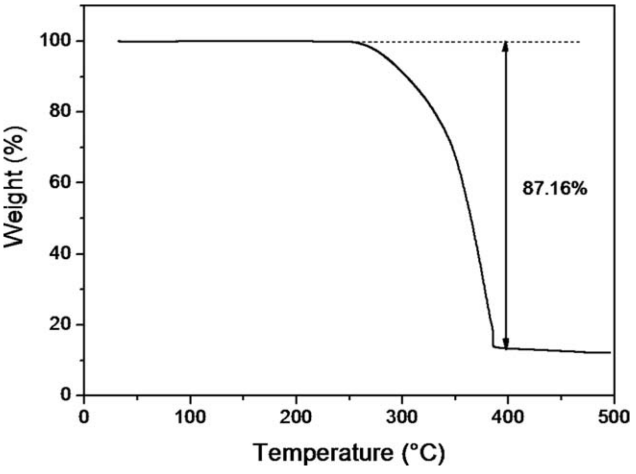

**Figure 4** TGA of polymer core for sandwich structures.

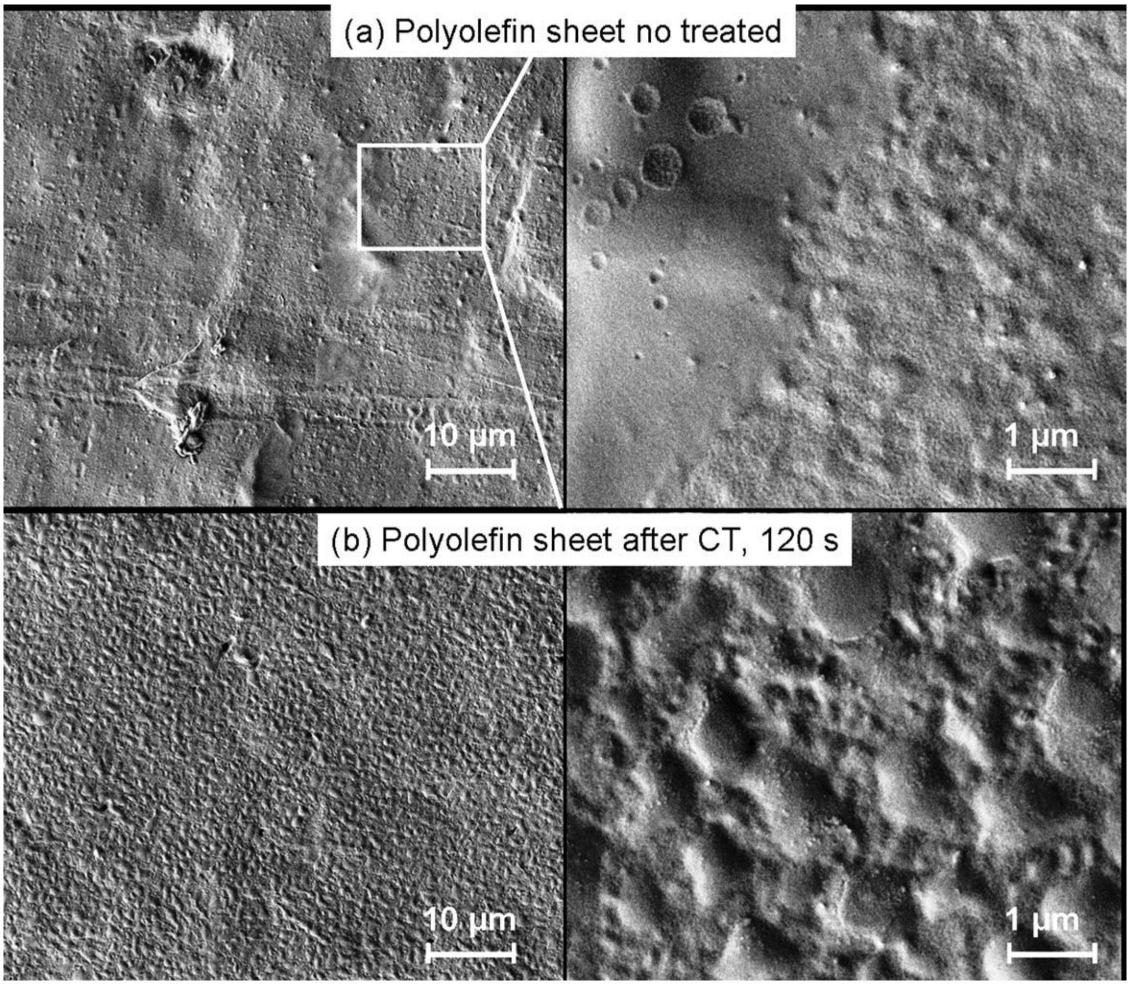

**Figure 5** SEM image of PO before (a) and after (b) corona discharge treatment after 120 s.[40]

corona surface treatment. These enhance the surface adhesion and wettability as stated by Zhang,[24] too.

As shown in Figure 5(b), CT changes the surface morphology of polymer. Roughness is increased by means of the surface activation. Moreover, the CTs oxidation process strengthens and prepares and improves the epoxy resin's adhesive behavior. As demonstrated, the effect of

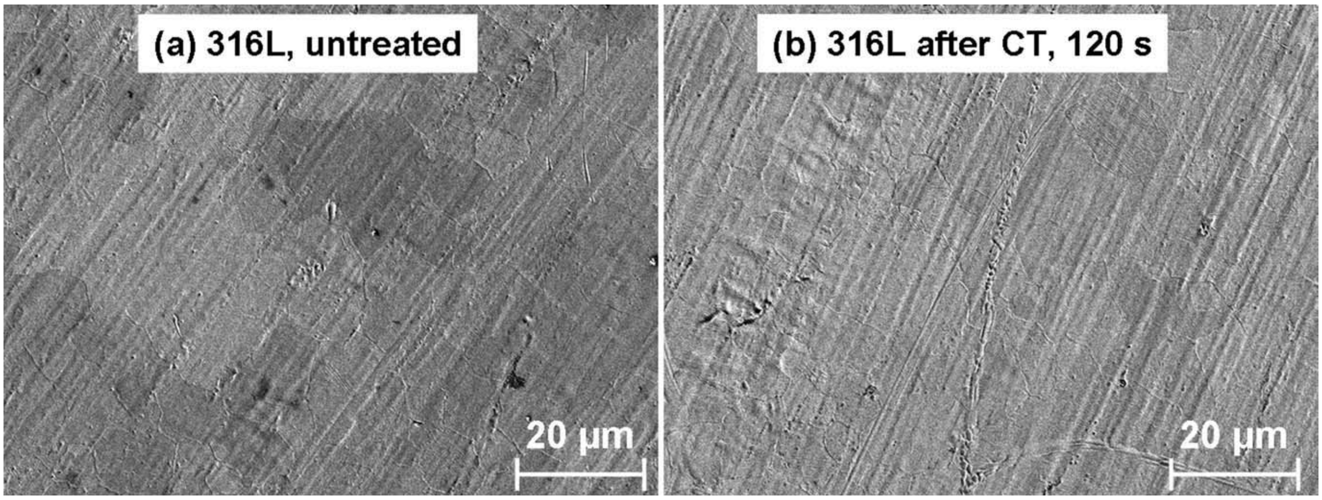

**Figure 6** EM images of the steel surfaces without CT (a) and with CT after 120s treatment (b).

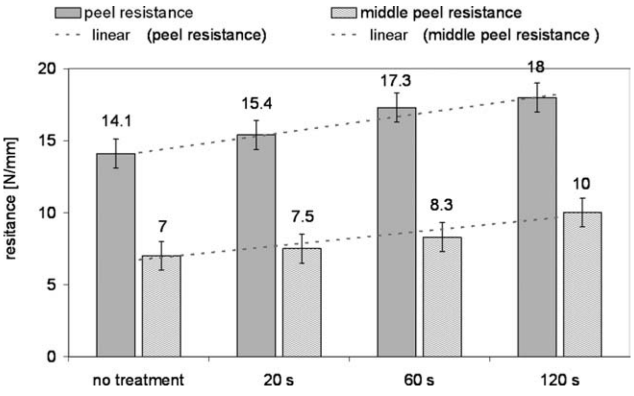

**Figure 7** Peel indexes of PO foil Corona treated for different periods (20, 60, 120 s). (Mean ± SDa standard deviation for $n = 6$). aSD, standard deviation.

corona strongly depends on the treatment times (Figs. 7 and 8).

Studying the mechanical properties of corona-modified PO in a MPML, it could be shown that treating of the sandwich sheets with corona on air resulted in an increase in sandwich strength (Fig. 9 and Table I). YS and TS have been found to be clearly affected by CT, indicating that these composite properties were highly sensitive to interfacial phenomena. However, elongation at rupture of composites was slightly decreased after CT. This follows the standard rules of mechanical behavior.

For MPML T_CT ($\alpha = 0°$), a pronounced improvement of 8% and 16% for TS and YS has been observed, respectively. Additionally, in the case of MPML L_CT ($\alpha = 0°$) and L_CT ($\alpha = 90°$), a slight rise of 4% and 6% (for TS and YS) was noted. On the other hand, for T_CT ($\alpha = 90°$) no variation could be discerned. Using CT, the composites' elongation at rupture has not significantly changed.

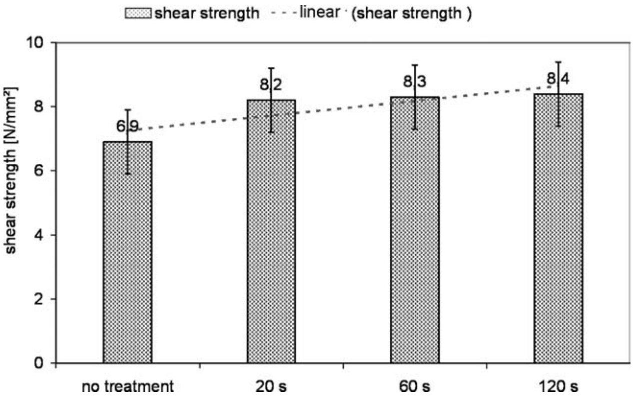

**Figure 8** Shear adhesion index for the different CT times for MPML (mean ± SD for $n = 4$).

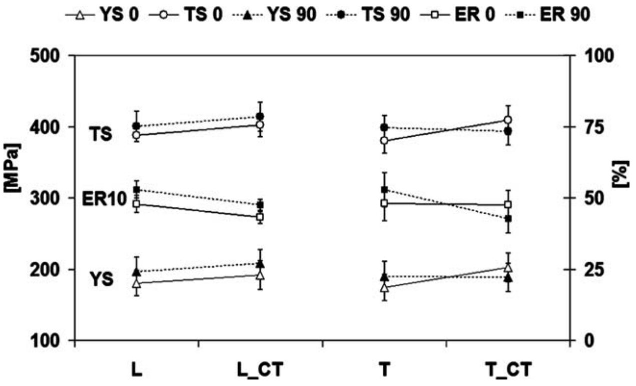

**Figure 9** Mechanical properties (YS, TS, and ER10) for specimens taken in the direction of roll bonding ("0") and in the transverse direction ("90"), as described in the insert Table I. (Mean ± SD for $n = 3$), "CT": PO sheets treated by corona.

## CONCLUSIONS

As presented here, CT can change the surface morphology only of polymer core of sandwich composite as well as introduce polar functional groups of PO onto the surfaces. The effect of increasing of polar polymer groups can be detected by increasing the adhesion between sandwich layers. No visible corona effect was detected on the steel surface morphology. The surface morphology is the key to understanding the changes in adhesive behavior of the polymer films during CT. Changes in the roughness of polymer surface caused by these processes can also affect the level of adhesion.

CT changes the surface morphology, the adhesion as well as the mechanical properties. It offers good possibilities for activating the polymer surface and for increasing the interaction between the metal and the polymer layers via the epoxy resin bonding. With this method, the adhesion between the layers of MPML is increased and CT, with its short process time of 120 s, can be used for industrial production.

**TABLE I**
**Tensile Strength (TS), Yield Strength (YS) and) Elongation to Rupture (ER10), all at Room Temperature, for Different Processing MPML (Figure 3) Under Three Angles α to Rolling Direction (RD) and with Treated and Untreated Polyolefin**

| Sample | α [°] | TS [MPa] | YS [MPa] | ER10 (%) |
|---|---|---|---|---|
| L | 0 | 388 ± 19 | 180 ± 18 | 48 ± 3 |
| | 90 | 400 ± 18 | 196 ± 16 | 53 ± 3 |
| L_CT | 0 | 402 ± 20 | 192 ± 20 | 43 ± 2 |
| | 90 | 414 ± 20 | 208 ± 18 | 48 ± 2 |
| T | 0 | 381 ± 21 | 174 ± 17 | 48 ± 6 |
| | 90 | 398 ± 19 | 190 ± 21 | 53 ± 5 |
| T_CT | 0 | 409 ± 22 | 203 ± 20 | 48 ± 3 |
| | 90 | 394 ± 20 | 189 ± 20 | 43 ± 5 |

(Mean ± SD for $n = 3$).

It is concluded that the CT represents a valuable strategy for surface modification, consistent with targeted mechanical properties of the composites.

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