LOW-PRESSURE PLASMA TREATMENT APPLIED TO POLYMERIC MATERIALS FOR A SUSTAINABLE FOOTWEAR INDUSTRY

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In this paper INESCOP proposes the improvement of the bonding of footwear soling materials using the low-pressure plasma surface treatment as a non-polluting and resource-efficient technology by means of adhesive bonds, with a reactive hot melt polyurethane adhesive, as a more sustainable alternative to current chemical surface treatments such as halogenation. More precisely, low-pressure plasma is capable of cleaning and removing all impurities, such as oxides, oils and fats on material surface. Then, it is activated by producing new chemicals species on the top layer of the substrate. Thus, the materials' surface acquires new surface functionalities, improving the compatibility adhesive-substrate and, therefore their adhesion properties. Furthermore, in this work the surface modifications produced in these materials of different polymeric nature have been optimised to increase their roughness, wettability, adhesive properties, etc., and have been validated through various experimental characterisation techniques. As a result, the samples treated with plasma meet the adhesion requirements for footwear materials. As a result, low-pressure plasma treatment has demonstrated to be a green, alternative, and sustainable technology in line with European policies on circular economy, which enhances material surface properties by improving the adhesion bonding process.

Keywords: bonding, sustainability, wettability

INTRODUCTION

The appearance of new materials for the manufacture of footwear and components, especially in the production of soles are mainly polymeric materials, which present excellent mechanical and aesthetical properties, but due to their low surface energy they show poor adherence to other components of footwear presents adhesion difficulties (Orgilés-Calpena *et al.*, 2019).

Currently the footwear industry is looking for environmentally sustainable alternatives that are already used in other sectors such as plasma technology. This is because until now to obtain strong and durable adhesive bonds, surface treatments with solvents and dangerous chemicals have been used that can suppose risks to the health of workers and the environment (Orgilés-Calpena *et al.*, 2018).

Plasma is considered the fourth state of matter, since it is a gas that is supplied with a continuous energy charge, ionizing it and electrically charging its particles. This process originates the so-called "plasma", which acquires a series of properties that do not exist in the other states of matter, being able to interact with the substrates with which it comes into contact. Thanks to the properties of plasma, it can produce different effects such as an ultra-surface cleaning, activation surface and surface etching of materials. This surface treatment can clean and remove all impurities, such as oxides and fats. Once the surface has been cleaned, it is activated by the production of new chemicals species of the gas introduced, which are attached to the top layer of the substrate. Then, the surface of the material acquires a new surface function, thereby improving the compatibility of the adhesive with the substrate and their adhesion performance (Tyczkowski *et al.*, 2005; Kapica *et al.*, 2019; Mandolfino *et al.*, 2019).

Therefore, this paper focuses on the study of the improvement of the adhesion with plasma technology in representative polymeric materials of the footwear industry, such

as thermoplastic polyurethane (TPU) and ethylene-vinyl-acetate based materials (EVA). Specifically the low-pressure plasma technology, whose effectiveness has been optimized by varying plasma processing parameters and analysed with different characterization experimental techniques.

EXPERIMENTAL

Materials

In this study, materials of different polymeric nature have been used as representative soling materials of the footwear industry. On the one hand, a thermoplastic polyurethane (TPU) and an ethylene-vinyl-acetate (EVA) have been used as adherents, and as an upper material, chrome-tanned leather split. On the other hand, a reactive polyurethane hot-melt adhesive has been used.

Low-Pressure Plasma Technology

To generate the low pressure plasma, a Tetra 30 plasma system has been used. The treatment is carried out in a chamber in which the samples are introduced and the vacuum process is carried out at 15 Pa. Then, a flow gas is introduced at a pressure of 30 Pa, and in this case, oxygen at a mass flow of 500 cm³/min. The gas enters the chamber through a high frequency electric field of 13.56 MHz and 300 W of maximum power (100%). The chemical radicals originated in this discharge react with the material's surface. In addition, plasma operating conditions, such as the exposure time range, have been configured between (30 to 300 s), and plasma power (from 50 to 100%).

Characterization Techniques

The effectiveness of the plasma treatment and chemical modification on the material's surface has been evaluated by different experimental techniques such as: Fourier Transformed Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), contact angle measurements (EN 828:2013) and surface energy measurement (Owens and Wendt, 1969). The adhesion performance before and after plasma treatment has been evaluated by the T-peel strength test of upper-soling joints obtained with the reactive hot melt polyurethane adhesive (EN 1392:2007; EN 15307:2015).

RESULTS AND DISCUSSION

In Figure 1, the infrared spectra obtained with and without the low pressure oxygen plasma treatment can be observed. The non-treated TPU and EVA samples show the most characteristic bands of both materials. According to the spectra obtained with plasma treatment, no significant chemical modifications were evidenced with respect to the untreated samples. (Enciso *et al.*, 2017; Sundryal *et al.*, 2020).

Figure 1. Infrared spectra of TPU and EVA with and without plasma treatment

The surface modifications produced on TPU and EVA surface by the different low-pressure plasma treatment conditions were analysed by scanning electron microscopy are shown in Figure 2. On the one hand, in the case of TPU, it is observed that the untreated sample surface is completely smooth and clean but in the plasma-treated samples, some roughness has been originated on the surface, making it less uniform. On the other hand, the untreated EVA surface shows a high porosity, which decreases after applying the plasma treatments that close the surface's pores and increase its roughness. In both materials, these effects might involve an increasement of the mechanical adhesion caused by an increased surface contact area regardless of the different plasma treatments applied (Tyczkowski *et al.*, 2005).

Figure 2. SEM images of non-treated and plasma treated samples of TPU and EVA

Figure 3 shows the contact angle values of the plasma-treated and untreated materials samples. The unmodified samples show high contact angle values in both materials, especially with liquid water, which means that the surface has low polarity and wettability, therefore a low surface energy. After oxygen plasma treatment, the contact angles measured using water as reference liquid are reduced due to the fact that

the polarity of the surface increases and slightly increases simultaneously the contact angle values obtained using the non-polar liquid diiodomethane (DIM) as reference liquid. This chemical and morphological effect in the polarity of the materials increases their wettability (Kapica *et al.*, 2019; Mandolfino *et al.*, 2019; Monzó-Pérez, 2015; Chen *et al.*, 2017).

Figure 3. Contact angle values obtained from materials studied.

According to the results obtained from the contact angles, the surface energy of each material can be calculated. This is shown in Figure 4 according to Owens-Wendt method. In both untreated materials, low surface energy values are obtained, in which the polar component is not appreciated. This indicates that it is a non-polar surface. Plasma treatment increases the surface energy values, whose dispersive component is decreased and polar component is increased in all the treatments. The chemical modification produced on the materials surface is translated into an increase in the polarity, wettability and compatibility of the substrates with the adhesive, particularly in the treatments in which the both components, nonpolar and dispersive are balanced, such as 30 s - 100% and 300 s - 50% for TPU and EVA, due to the need for a balance of polarity on the surface (Yáñez-Pacios and Martín-Martínez, 2018; Ngoc and Thai, 2017; Arán-Aís *et al.*, 2020).

Figure 4. Surface energy values obtained from materials studied

The effect of oxygen plasma treatment on the adhesion properties of the considered materials, TPU and EVA respectively, was evaluated by means of T-peel strength assays using split leather/reactive polyurethane adhesive/plasma treated and untreated

TPU or EVA joints. Before joint formation, EVA and split leather samples were duly roughened.

Figure 5 shows the T-peel strength values obtained after 72 h of the joints formation. The effect of low-pressure plasma treatment on the bonding properties of treated bonds caused a noticeable increase in the adhesion compared to control samples. This improvement of the adhesion properties can be attributed to both an increase in surface roughness the increase in surface energy, respectively. According to the results, the highest value obtained in TPU bonds corresponds to the lowest exposure time (30 s) and the highest power (100%). In addition, in EVA bonds is observed that the best result corresponds to the highest exposure time (300 s) and the lowest power (50%). Both plasma treatments described indicate that these parameters increase the low-pressure plasma effectiveness, which is also verified in the case of EVA rubber by a change of the failure type from a mixture of adhesion failure and superficial exfoliation (A2/S2) to superficial exfoliation (100S2), indicating increased bond strength adhesive-substrate. Otherwise, with TPU, the type of adhesion failure (A2) is the same with and without plasma, therefore, it is not modified due to the nature of the material that is more resistant, however, there is a marked increase in the bond strength (Tyczkowski *et al.*, 2005; Kapica *et al.*, 2019).

It should be noted that all cases in which oxygen plasma treatments have been applied improve the adhesion of the bonds studied and exceed the minimum quality requirements demanded for footwear according to standard tests (EN 15307:2015; Arán-Aís *et al.*, 2020).

Figure 5. Comparative graphs of T-peel strength values of leather/HMPUR adhesive/TPU and EVA joints after 72 h with and without oxygen plasma treatment. Failure type: A2: adhesive failure of the TPU. S2: superficial exfoliation of the EVA.

CONCLUSIONS

According to the obtained results with the application of the different low-pressure plasma surface treatments on the TPU and EVA. It is concluded that when there is an increase in roughness, there is a decrease in the contact angles that results in an increase in the surface energy, which is mainly due to the increase in polar component rather than the dispersive one. Consequently, leading to an improvement in the final adhesion properties of the considered adherents, that allows fulfill minimum requirements for the upper-to-sole joints for footwear applications.

In short, plasma technology is an innovative technology and its implementation in the bonding processes of the upper-soling joint in footwear will contribute to the

development of a sustainable footwear industry in line with the circular economy and the European sustainability policies, such as the Green Deal, as well as the achievement of the sustainable development goals.

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