

WORLDFOOTWEAR

Plasma technology for preparing soles

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Manufacturers in all sectors have become obliged by law to reduce their emissions of Organic Volatile Compounds (VOCs). In the footwear industry, one of the main sources of VOCs is the process of cementing soles for attachment to the lasted upper. While in many cases it is possible to use water-based adhesives, the bonding surface must still be prepared using a halogenisation process.

The legal restrictions on the emissions on this type of process are quite severe at 20 mg/m³ for consumption beyond 100 g/h, so CTC decided to test an alternative, dry-process technology, plasma. After successful initial tests on TR and SBR soling materials, a second trial has been carried out on polyamide (PA) and PEBA, which are far more difficult materials to prepare. The initial findings of this further trial again confirm the suitability of this technology for the preparation of soles prior to applying the actual adhesive.

BACKGROUND

The objective of the EU directive, dated March 11, 1999, was to reduce and control the emissions of VOCs caused by the use of organic solvents in manufacturing processes. Since October 2005, it has restricted the solvent consumption for footwear producers using over five tons per year to no more than 25 grams per pair of shoes.

Soling adhesives are one of the main sources of solvent use in the footwear manufacturing process. However, the cleaning and halogenation treatment of the bonding surfaces of the soles themselves ready for application of adhesive also requires the use of solvents and chlorinated (halogenation) products.

Certain types of soling materials such as TR, rubber, EVA, polyamide (PA) and polyether block amide (PEBA), normally require this type of surface treatment. For example, materials containing a plasticiser are difficult to bond because these additives do not have a good wet-ability with the adhesive. The intrinsic chemical composition of certain other soling materials



may also make them incompatible with normal adhesives.

CTC therefore set out to see whether plasma treatment might be a viable alternative to traditional solvent-based systems and overcome some of these problems. Having already proved the effectiveness of plasma treatment on more commonly used materials such as SBR and TR, the aim was now to test its effect on more difficult materials such as PA and PEBA where a chemical treatment is essential in order to obtain effective adhesion between sole and upper.

POST-DISCHARGE COLD PLASMA

As with all surface treatments, the aim is to trigger controlled degradation of the surface via a chemical action that will react with the adhesive to create chemical bonding and/or polarisation in order to increase thermodynamic adhesion.

Plasma—otherwise known as the fourth state of matter—is a partially ionized gas made up of molecules and fragments of neutral gas, free electrons, cations (positively charged ions) and disturbed molecules that return to their fundamental state and emit electromagnetic radiation.

Cold plasma refers to non-thermal plasmas that appear under reduced pressure. Although the treatment is referred to as being a plasma, the material being processed is not actually subjected to a plasma as it is not placed between the electrodes in the discharge but in post-discharge and because the resulting flux contains only non-charged particles.

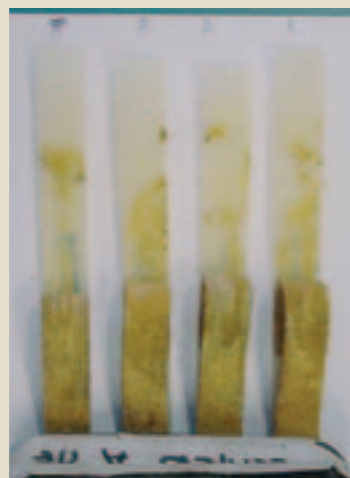
TESTING PROCEDURES

In order to quantify the effects of cold plasmas, comparative trials were carried out with some materials receiving plasma treatment and others simply a normal mechanical preparation. The test pieces were then bonded to a standard leather.

It must be appreciated that plasma technology enables a certain number of parameters to be adjusted in order to optimise its use:

- Type and proportions of gas (pure nitrogen, nitrogen + oxygen, nitrogen + hydrogen, nitrogen + carbon dioxide, etc)
- Distance from plasma source
- Throughput

Peeling test on PEBA



POLYETHER BLOC AMIDE (PEBA)

This material is frequently used for the soles of football and other specialist sports footwear and is it is very difficult to avoid using phenol-based primers in order to obtain a good bond. Testing showed that overall and, whatever gas mixture was used, average strength values were far superior to those achieved on test samples prepared mechanically and without plasma treatment.

The nature of the adhesive joint break obtained reveals enhanced adhesion between the polymer and the adhesive compared to non-treated samples.

POLYAMIDE (PA)

PA is also used for rigid soles on athletic shoes and football boots, and also requires a phenol-based primer prior to applying an adhesive.

Whatever the gas mixture used, the bond strength values obtained were greater than those of the control samples. For

Peeling test on polyamide



nitrogen and hydrogen, they were clearly much better and superior even to those obtained when using a mechanical preparation such as rough scouring or roughing.

CONCLUSION

Cold plasma treatment in cold discharge clearly makes it possible to obtain stronger adhesion of polyamide and polyether bloc amide without using a primer type product. The results obtained in the tests carried out so far are all the more encouraging in that this has only been a pre-feasibility study and the process has not yet been fully optimised. The throughput factor in particular must be optimised in order to establish a maximum speed that will also offer maximum efficiency and eliminate the thermal effects responsible for

phenomena such as plasticiser migration. This compromise will also depend on the material in question and the composition of the gas used. 

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