

INTRODUCTION

Flame treatment is an industrial process used to improve wetting and adhesion properties of polyolefin films (BOPP Bioriented Polypropylene; OPP - Oriented Polypropylene; PE, PET, PS, etc.) and 3D components, such as automobile body parts (bumpers, dashboards, headlights, etc.) and blow-molded bottles.

Polyolefin materials, and in particular PP (polypropylene) have many good properties as: low cost; can be worked and shaped quite easily; can get good mechanical properties, if properly worked; are very good electric insulators.

Anyway they are apolar on their surfaces, which are characterized by very poor energies. This is the reason why they need to be treated, in order to make possible their coating with inks, paints, adhesives, metal, and other materials typically coupled with polyolefins, in industrial applications as flexible packaging or automotive production.

FLAME CHEMISTRY

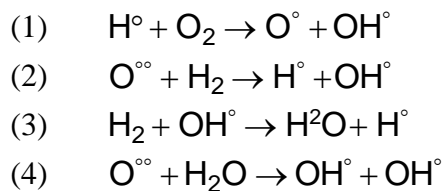
Activation of polyolefin surfaces by flame is realized by means of two actions:

- breaking of carbon - hydrogen links along the polymer surface, thanks to flame high temperature, developed by the combustion process. Theoretical temperatures, reached using C₁-C₃ hydrocarbon combustibles, are between 1700 °C and 1900 °C. As first step in the surface oxidation process, hydrogen abstraction is far the more likely one, in comparison with breaking of a C-C link along the macromolecular backbone. Links C-C type are infact shielded, from radicals external attacks, by means of hydrogen and metyl groups surrounding the molecule backbone (cage effect). In addition, the mobility of radicals -C° type, coming from an eventual scission of C-C links, is really reduced (because of radicals -C° dimensions), so high is the probability of a recombination, after the scission, between radicals -C° and °C-.

- Insertion of oxygen based groups – contained inside the flame area - in correspondence of broken links points, along the macromolecular chains. The oxygen so transferred to the polymer surface acts as a bridge between the polymer itself and the second material to be coupled with it.

Premixed laminar flame - in which the fuel and the oxidizer are thoroughly mixed prior to combustion - is produced by radical/chain reactions occurring in a combustion system, formed by an oxidizer (generally air) and a combustible (in a solid, liquid or gaseous state). Here will be considered just the last case, being only gaseous combustibles typically hydrocarbons (natural gas, methane, propane, LPG, etc.) – used for polyolefins surface flame treatment.

Chain branching step produces a radical pool, according to the following oxyhydrogenation reactions:



The sequence [Eqs. (1) - (4)] is of great importance in the oxidation reaction mechanics of any hydrocarbon, in that it provides the essential chain branching and propagating steps as well as the radical pool for fast reaction to occur.

It is this radical pool that develops the oxygen based groups inside the flame, used to activate the polyolefin surface (2nd factor of action of the flame). First factor being flame temperature.

BOPP SURFACE FLAME OXIDATION MECHANISM

BOPP surface oxidation by flame is in Literature defined as a Free Radical Degradation, beginning with radicals attack on tertiary carbon of the macromolecular backbone. The initial step in oxidation of polymers by a flame is so passing through polymer-radical formation by hydrogen abstraction. H abstraction along macromolecular chain is far more likely to occur respect to carbon-carbon link breaking, because of cage effect exerted by methyl and hydrogen group towards C-C link and because of lack of mobility of the C atoms, after the link breaking, so they form again the link. Polymer-radical formation occurs primarily by reaction with the O atoms, H atoms and OH radicals found in

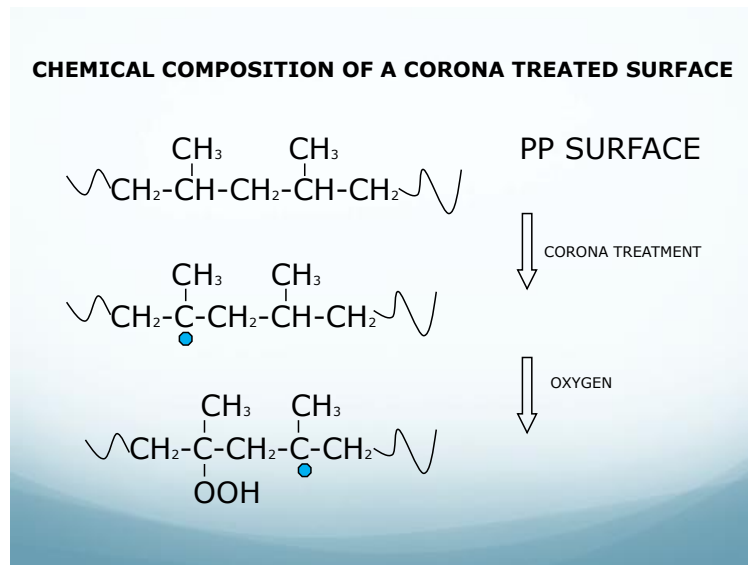
the flame. Thermal energy from the flame could also generate polymer radicals (alkyl radicals R). Hydroxyl OH radicals are considered from literature the ones playing most important role in the film surface oxidation, since are the ones characterized by highest concentration and highest reactivity (reaction rate constant for OH radical is at least two order of magnitude higher than the ones of the other radicals present in the flame, as molecular and atomic oxygen radical or peroxy radical).

H radicals will tend to compete with the OH and O species terminating the oxidation step, so, basically H tends to compete to generate less wettable PP surfaces.

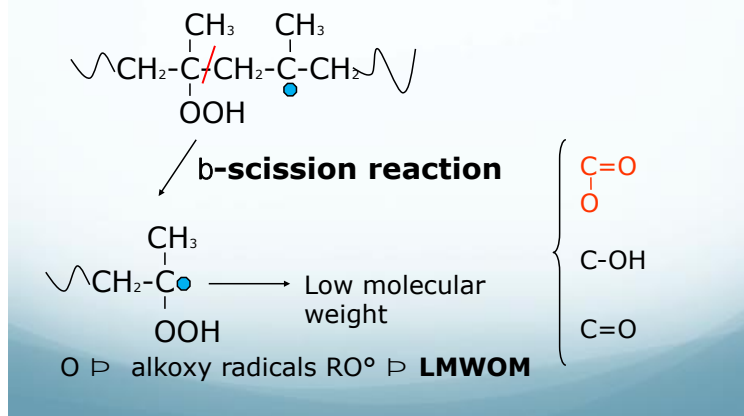
A COMPARISON WITH CORONA TREATMENT

When using flame, the depth of Oxygen incorporation in the treated PP is between 5 and 10 nanometers versus a depth of about 50 nanometers in case of corona treatment. So with flame there is a more extensive oxidation concentrated in a shallower surface region, that results in an higher wettability.

Corona treated PP (and in general polymers as PET, PE, and others) are characterized by the presence, on their surface, of LMWOM. This presence is much higher when increasing corona watt density applied to the material (literature refers this as overtreatment). LMWOM stands for Low Molecular Weight Oxidized Materials. These oxidized materials are produced on corona treated PP surface because of C-C links breaking (this reaction is known in literature as β -scission reaction) and consequent weight lowering.



CHEMICAL COMPOSITION OF CORONA TREATED SURFACES



LMWOM are oxidized materials water soluble or other solvent (as acetone or methanol) soluble and generally more weakly anchored to the PP surface. Atomic oxygen radical is the precursor of LMWOM formation, passing through alkoxy radicals (RO) formation. Literature states that when an hot flame impinges the cold (at about 400 K) PP surface, many radicals present in the flame (that is produced by a radical reaction) are destroyed. This destruction doesn't affect OH radicals concentration – since they are far the more present radicals in the flame, but there is a big impact on atomic oxygen radicals, that strongly diminish their concentration. The following formation of alkoxy radicals – from which LMWOM develop – is so negligible in case of flame; with flame LMWOM could eventually form (as an alternative way respect to the one represented by RO radicals) starting from carboxylate/peroxy groups (COO), but these groups scission to form alkoxy groups is too slow to account for a significant formation amount of LMWOM. Moreover formation of COO groups can be kept under control with flame, working with an air/gas ratio not too gas lean (so not too oxygen rich). The same phenomenon doesn't occur with corona treatment, where alkoxy radicals, that are present in a large extent, are involved up to 50% in the β -scission reaction types, so forming LMWOM. In a PP flame treated surface, instead IMWOM (Intermediate Molecular Weight Oxidized Material) are present, that are bigger than LMWOM, with higher weight, not soluble to water and other polar solvents and so more strongly anchored to the PP surface. This fundamental difference between corona and flame treatments, along with the fact that corona produces a deeper treatment than on a web treated by flame, is the cause for an

higher surface energy of a flame treated film than a corona treated one. Among web producers there is the folk to measure the wettability after treatment on the web, through the specification ASTM D2578. This test is very simple to perform, very fast also and can give to the operator immediately the idea if his machine is correctly working. By the way ASTM D 2578 doesn't tell everything about the web surface after treatment.

Two films having same ASTM D2578 dyne level can have a huge difference in terms of surface energy. And what really cares in terms of processability of the web after the treatment is the surface energy it has, not the wettability.

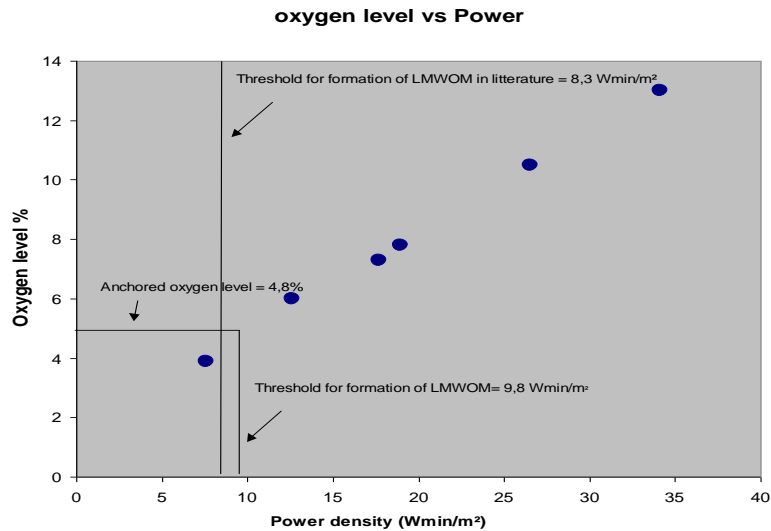
A corona treated web can show a good wettability, thanks to the presence of oxidized material on its surface (LMWOM), but these materials are weakly tied to the film surface, so they are easily taken away from the surface itself, according to typical delamination phenomenon.

This means that using corona you get a good fresh (on line) treatment, but then you get a poor treatment for applications as printing, laminating and metallising and you get a strong decay of treatment (aging phenomenon) few weeks after the treatment. Flame treatment is characterized by an higher anchored oxidation type of the polymer surface, than the one possible treating the web by corona, as measured by ESCA (XPS-X ray photoelectron spectroscopy) technique.

Using corona treatment is possible to get, as shown on the above slide an oxygen level % measured by ESCA in the order of 14 and higher (see below image), increasing the treater watt density; but just a minor amount - about 5% is the anchored one; the rest is given by LMWOM. In the case of flame treatment all the oxidized material is well anchored on the film surface.

This difference is well underlined by a simple test: water washing of corona and flame treated samples. Surface chemistry of corona treated film is strongly affected by water washing, with a significant loss of surface oxidation and a noticeable increase in the advancing contact angle of water.

Corona treated surfaces have an O/C ratio, at ESCA, up to 0,23, becoming, after water washing, 0,08. In the case of flame O/C ratio is 0,18 before washing and still 0,18 after washing. This is a clear evidence of the presence of water soluble LMWOM on the corona treated PP, while flame treated PP has no detectable LMWOM, since the O/C ratio does not vary with the water washing.



Basing on this difference in surface chemistry and in surface energy, after flame treatment and after corona treatment, much different is also film behaviour in its performances. Presence of LMWOM first of all can explain higher treatment decay observed in corona treated surfaces, respect to flame treated ones. Treatment decay or aging depends much also on film composition and additives presence inside it, but, considering same type of film, corona treated will always decay faster than flame treated, because of the presence of the above reported LMWOM.

FLAME TREATMENT APPLICATIONS ON MET AND PRINT BOPP

Metallised film after corona will present poor performances both in terms of barrier to water vapour and to oxygen if compared to the ones of flame treatment. Also metal adhesion after flame will be at least 30% higher after flame than after corona and also much more lasting with the time. This last difference is well underlined by REXAM tests, from which it is possible to see that starting metal adhesion to substrate is much lower and also much faster dropping when film is corona treated than one it is flame treated. This is confirmed by the fact that if flame treated film is then corona treated (for example for refreshing treatment, as in use in many converters facilities) REXAM test will give poor adhesion of the metal if compared to the adhesion coming from just flame treated film. This because corona is introducing LMWOM materials on the flame treated surface, modifying its chemistry.

For printing applications particularly significant to explain the difference in surface adhesion between corona and flame treatments is the results of an experimentation run in esseCI lab. Different samples of the same film, both corona and flame treated were analysed. The corona and flame treated samples presented same treatment level, according to ASTM D2578 specification.

On the two samples series (flame and corona treated) were then spread different types of Sun Chemical inks (Demachem, Multilam), nitrocellulose based inks, modified using polyurethanes resins, by means of a metering rod (wire size 06), according to TAPPI T552pm-92 specification. The samples were then dried, cured in an oven equipped with a forced air circulating system, at 70°C for 10 seconds, as per the ink producer recommendations. After the samples preparation, these were used in two kinds of tests:

1. manual peeling test: according to the inks producer specifications was performed both slow and fast peeling, using an ASTM tape, 45° inclined respect to the sample surface;
2. automatic peeling test: using a tensile strength testing machine (dynamometer) – Zwick Roell type – in order to measure the adhesion strength of the samples. The ASTM tape has been fixed at one clamp of the dynamometer, and the sample on the other clamp.

The inks used in the tests are generally used with a diluent (ethyl acetate) and an adhesion promoter. In the case of the test here reported no adhesion promoter has been used, to underline the film treated surface strength and energy, coming just from the surface treatment (corona or flame), so to check just the treatment contribute to adhesion. Absolutely macroscopic is the difference in behaviour between corona treated and flame treated surfaces, both in the manual and in the automatic peeling test, in terms of ink surface removed by the tape, and in terms of bond strength (in case of flame treated ink/film bond strength keeps around 400g; with corona treated samples well lower than 200g).

Printing

FLAME vs. CORONA SURFACE ADHESION

CORONA TREATED - SLOW PEELING



FLAME TREATED - SLOW PEELING



CORONA TREATED - FAST PEELING

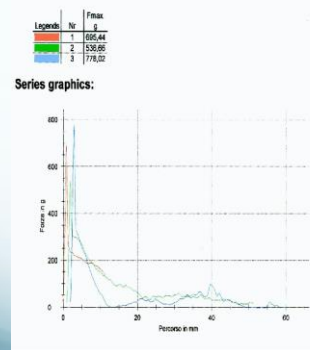


FLAME TREATED - FAST PEELING

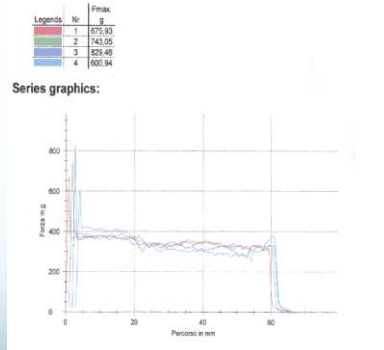


FLAME vs. CORONA SURFACE ADHESION

CORONA TREATED



FLAME TREATED



In the below image, the samples (film + tape) on the top were coming after corona treatment, while the samples on the bottom after flame treatment. It is evidenced how in corona treated film, ink has moved from the film to the tape, while in flame treated film, it has been the tape glue to move from the tape to the ink, thanks to film high adhesion values.

FLAME vs. CORONA SURFACE ADHESION



CONCLUSIONS

Actually flame treatment technology is a mature one, but still characterized by high improvements margin, as last process developments are demonstrating.

There is no machine able to do everything. Starting from this consideration, it is anyway out of any question that flame treatment can warrant higher quality on film treated surfaces, thanks to its higher surface adhesion and surface energy. This is particularly true in applications as:

- metallisation: where flame treated surfaces, compared to corona, allow significantly increased barriers to water vapour (WVTR) and to oxygen (OTR), as well as improved and longer lasting adhesion of metal to the film, as widely demonstrated by REXAM tests;
- printing/lacquering: where flame treated surfaces allow, compared to corona, to get better printing quality, improved toner adhesion and improved visual quality, as well as improved rub-off and abrasion resistance in flexo, rotogravure and digital printing applications;
- tapes films.

When treating heat sealable film, flame treater presents a narrower working range and, depending on process conditions and film type sealability on treated/treated sides (TR/TR or external/external) can be not as good as when corona is used.

Concerning this point it is important anyway to underline the following: in the flexible packaging industry treated/treated or Ext/Ext sealability is requested only in uncommon applications (as overwrapping just for certain kind of biscuits and tobacco films) or to form bellows. In these cases it is not requested an high sealing strength, since the resistance of the package is given by the paper pack, wrapped by the sealing.

So in these cases flame can warrant requested sealing strength also on TR/TR sides. On all the other flexible packaging applications Fin Seal (sealing is on untreated/untreated, that is internal/internal side), is always used when Horizontal Form Fill Seal (HFFS) machines are run (for example with biscuits or long pasta as spaghetti). In the case of snacks or short pasta used is Lap Seal with Vertical Form Fill Seal (VFFS) machines, where the seal is on treated/untreated sides, so external/internal.

In Fin Seal and Lap Seal cases, that are the far majority in flexible packaging applications, as it is possible to see visiting a food market, flame can warrant better results than corona, since it doesn't affect, despite corona, the untreated side of the film. In the case of chips are used VFFS machines, but with laminates structures, where printed/treated sides are placed internally, so they do not interfere with sealability.

In not so common application also a lacquer layer is used on the sides to be sealed, in this case, again, no issues on sealability coming from flame treatment.

So, flame treatment issues with sealable films is a false problem, in the name of which makes no sense to renounce to the higher performances of flame treatment over corona treatment as above described.

This is the reason why on an high performances 5-layers BOPP extrusion line flame treatment has to be present, in bottom position (corona on the top), for getting best results on all produced type films.

REFERENCES

- [1] Lori G. "Aspetti chimico-fisici nell'attivazione di superfici mediante il trattamento alla fiamma" (1985).
- [2] Strobel M., Branch M.C., Ulsh M., Kapaun R.S., Kirk S., Lyons C.S. "Flame Surface modification of polypropylene film". J. Adhesion Sci. Technol. Vol.10, No.6 (1996).
- [3] Strobel M., Sullivan N., Branch M.C., Jones V., Park J., Ulsh M., Strobel J.M., Lyons C.S. "Gas phase modelling of impinging flames used for the flame surface modification of polypropylene films". J. Adhesion Sci. Technol. Vol.15, No.1 (2001).