PLASMA PRETREATMENT OF POLYMER WEB TO INCREASE THE QUALITY OF COMMODITY GRADE PACKAGING FILMS: AN ADHESION PERSPECTIVE

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Dr. David Wickens, R&D.
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Outline

• Plasma pretreatment background
  • Relation to adhesion
• Adhesion- testing methods
• Results from Bobst machines
  • Gas flow
  • Power
  • Gas type
• Summary/ Conclusions
Plasma treatment of commodity grade PET film in a production scale machine, at similar speeds to “customer machines”
PLASMA PRETREATMENT
Plasma Treatment

- Cleaning:
  - Neutralisation of the surface, releasing charged particles and removal of organic contamination
  - Removal by volitisation of oligomers
  - Ablation, microetching, scission, crosslinking and functionalization
  - Modification of the surface chemical structure
  - Sputtered seeding layer providing nucleation sites.
Why do we plasma pre-treat?  
What does it do?

Altering the surface of the film allows:

• Cleaning
• Increased Adhesion
• Improvements in coating uniformity (more wettable)
• More economical on the aluminium process
Surface alteration of polymers using plasma treatment

- Mass loss over time as the polymer chains are broken into shorter groups.
- This can produce a practical advantage but overexposure can lead to a layer of low M/W groups on the surface = poor adhesion to the polymer bulk.

Plasma treatment in a Production Machine.

Speeds commonly in excess of 400 m/min.
2x 110 mm wide electrodes.
Plasma treatment optimisation is essential to effectively create a substrate surface that creates high adhesion (in this case).
The short dwell time = essential for plasma to be optimum condition for the best treatment of the film.
ADHESION

INDUSTRY STANDARD METHODS FOR DETERMINING ADHESION IN PRODUCTION
Adhesion and why do we want it?

• What is Adhesion?
  • “The sticking together of particles of different substances”

• The strength of which the deposited aluminium layer is attached to the [polymer] substrate

Why?

• The films subsequently undergo converting processes
  • Slitting, laminating, printing
  • Contact with the film: damage
  • Delamination of the film during a lamination process would eliminate barrier benefits of the Al.
Ways to Improve Adhesion

• Chemical treatment:
  • Co-polyester or acrylic layer: 10-100% increase in £
  • Chemical treated film + Plasma = barrier reduction-trade off

• Polymer modification:
  • Low SIT polymer layer @ surface (more £ and sacrifice Barrier)

• Plasma:
  • Typically plasma in the market provides around 1-2N/15mm
  • Higher power creates a range of 2-4 N/15mm on PET
  • Atmospheric plasma
  • Flame treatment
Testing for adhesion
Tape test

- Tape with a specific adhesion characteristic
  - Scotch 610 Tape
- Stuck to the metal side of the film
- Removed at a 180° angle
- Removal of metal = fail / poor adhesion
- Qualitative test
- Fast, cheap, easy
- Basic test, only pass/fail
- Some samples pass tape test and fail the EAA Adhesion method…
Peel test
Heat sealed

European Metallizers Association (EMA) method
Follows ASTM F88, F904, ISO 11339-2005
Heat sealable EAA (Ethylene Acrylic Acid)
Pulled at a constant speed 180° angle.
Bulk failure during peel = coating adhesion.
Failure modes
Metal removal
EAA Heat seal Adhesion Test

- EMA procedure
- ASTM F88/F88M-09
- ASTM F904-98
- BS EN ISO 11339:2009
- Common in the market
- Relatively easy to perform
- Provides a satisfactory amount of information for the film producer on adhesion.

Adhesion test Background
EAA Adhesion test.

Adhesion characterisation:
Open to user interpretation
- Average value including whole peel test
- Average value of just failure area
- Maximum peel force from the film

Improved characterisation for future work:
- Maximum value
- Failure value (bulk peeling force average)
- If no failure the average value is taken and maximum force.
  - Low initial peel force followed by low peel force for the full peel area
  - High initial peel force followed by low peel force for the full peel area
  - High initial peel force followed by high peel force for the full peel area
  - Extremely high adhesion at the interface from EAA to metal resulting in failure if the EAA with no metal removal at level of 6-7N/15mm.
Solvent-based Adhesive Lamination

Adhesion tests

- EAA not a typical representation of one of the constituents of a common laminated pouch
- Replicate the conditions the film would go through in lamination process for packages and test the adhesion
- Metallised film gets a layer of solvent based adhesive
  - Sealant web is “laminated” on top
  - Sealant web is peeled off in the same fashion as the EAA trials
- Allows higher adhesions to be measured
  - Thicker film-less stretch at higher force
  - More suitable to measure wet adhesion
Comparison of Methods

Tape test:
• Incredibly quick and easy
• Instant results
• No dedicated lab
• Same tape used in most QA labs
• Very qualitative
• Only a pass/fail

EAA:
• Standardised procedure
• Gives lots of information
• Quantitative over the peel area
• Lengthy
• No heat sensitive samples
• Requires a lot of expensive equipment

Solvent Based Adhesive Lamination:
• Recreates what the coating will do in a lamination structure
• Best for wet adhesion tests
• Suitable for heat sensitive samples
• Requires skill
• Lengthy process
Comparison of Results

Tape test:
• Pass
• No Al pickoff observed

EAA:
• Average 3.77 N/15mm
• Average comparable to SBAL
• Peel profile completely different
• Cohesive peel with material break (indicated with red line)

Solvent Based Adhesive Lamination:
• Delamination of Al from substrate
• Average peel 3.77 N/15mm
TRIALS
Film Used in these investigations

- 12 micron PET
- Trias Sentosa ASTRIA 12 \( \mu \text{m} \) BOPET
- Common commodity grade packaging material
- PET is more difficult to get adhesion using plasma pretreatment
  - High melting point
- Adhesion on PET = easier to optimise on other films.

Source: http://www.trias-sentosa.com/
Platform Used
k5000

- Standard Bobst K5000
- 2450 mm width machine
  - Planar plasma pre-treatment
  - AlOx
  - Hawkeye® Monitor System
- Speeds up to 1000 m/min

Full size machine used purely for research and development of the standard platforms in Heywood, UK
Plasma treater Design.

- “Magnetron” Design
- Water cooled magnetic array
- Two electrodes
- AC configuration
- Standard up to 30kW
- Optional up to requested power of customer.
Gas Flow Argon
Gas flow in relation to adhesion

- Increase in pressure in the plasma zone causes the adhesion to decrease.
- Lowest gas flow performed best.

Argon:
- Process gas used for sputtering.
- High molecular weight to give high bombardment of the cathodes and of the substrate (film)
- Sputtering of the electrodes will not deposit much but will aid in reducing racetrack contamination and increasing stability.
Power
Using two different machines

Constants:
• Line speed
• Running conditions (relative to the machine type)
• Gas type (Oxygen Argon mix)
• Film type (batch) 12 micron PET

Limiting factor:
• Power maximum (customer machines/specifications)

Machine 2 optimised plasma treatment with latest developments being used
Scanning Electron Microscopy
Uncoated, plasma treated film
Scanning Electron Microscopy
Plasma treated film (at production conditions)
Methods for Characterising surface morphology of plasma treated PET

- AFM:
  - Nanometre resolution (nanotopography)
- XPS: Surface chemical composition
- Contact angles of solvents
  - Surface charges
  - Arguable whether this relates to adhesion
  - Suggests what species are on the surface and the surface only.
• Added increasing ratios of oxygen gas into the treater
• In this case more oxygen reduced adhesion
• No significant difference
• Literature suggests oxygen plasmas enhance adhesion.
  • May become apparent if there is a longer dwell time.
• Depending on the chemical makeup of the PET could affect the amount of oxygen required for optimum adhesion.
• Reactive gases, such as oxygen can be used to improve other process benefits of the film, besides adhesion.
• Water contact angle changes with different Plasma treatments
• Different gas ratios introduced
  • 100% Argon
  • 60% Argon, 40% Oxygen
  • 100% Oxygen
• Adding oxygen to the plasma decreased the contact angle (more wettable)
• Contact angles/ dyne levels arguably do not relate to adhesion.
• Adding oxygen appeared to decrease the
Cross Web Uniformity Example

- 1250mm wide film
- Measurements every 50 mm
- Duplicate peel tests for every sample.
- Trend suggesting the adhesion is greater closest to the pump side.

New technology looking into increasing uniformity.

#To be added
Conclusions

- In a large scale environment it is challenging to characterise what is happening analytically on the surface of the film
- However, differences observed in adhesion
- Look at the end product and what is happening
  - Adhesion tests: Tape, heat sealed & laminated
  - Quality control
- Optimisation based on film recipe and running conditions.
  - Different films will require different plasma treatment regimens.
THANK YOU FOR YOUR ATTENTION!

David Wickens
Bobst Manchester
Email: David.Wickens@bobst.com
Tel: +44 (0)1706 363 628