Ultra Versatile Adhesives to broaden the possibilities of Extrusion Lamination

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ABSTRACT

For the development of new structures by extrusion lamination, the question of finding suitable adhesives often remains a tricky limitation: lack of versatility in adhesion, lack of flexibility in processing, difficulties in purging, need of primers are some of the issues that converters would like to overcome. To these questions, the original chemistry of ethylene – acrylic ester – maleic anhydride terpolymers brings attractive answers. Versatile in processing and in adhesion, these functional polymers are considered with a growing interest in the very demanding industry of extrusion lamination. The first part of this presentation will focus on their properties, their processing, and the new solutions that they offer to the lamination industry. The second part deals with a topic of common interest for many people involved in multilayer design or manufacturing: understanding peel strength measurements, particularly the influence of multilayer structures.

INTRODUCTION

Extrusion lamination is an attractive technology combining performance and quality, without any solvent involved or any curing time to wait for. A big limitation is however related to the time it takes to reach steady running conditions and this is often related to the purging difficulty with many specialty resins, making transitions too long for short production runs. Another limitation is the lack of really versatile adhesives, easy to process, easy to purge, not corrosive and processable over a wide range of temperature. Regarding this, the main resins used in extrusion coating/lamination can be reviewed as follows.

- LDPE is of course the reference in processability, but its adhesive possibilities are limited to cases of miscibility and to aluminium foil thanks to melt oxidation.
- EVA copolymers or EVA-acid/anhydride terpolymers introduce some polarity or reactivity for stronger interactions, but limitation in processing temperature before degradation is a strong drawback.
- Acid copolymers EAA or EMAA are very efficient adhesives for aluminium but give no adhesion to oriented plastic films; they do not accept high processing temperatures and remain difficult to purge.
- Ethylene - Acrylic Ester copolymers like EMA or EBA are easily processable but their adhesive possibilities remain limited as well.

ETHYLENE – ACRYLIC ESTER – MALEIC ANHYDRIDE TERPOLYMERS

Introducing maleic anhydride as third and reactive comonomer in an ethylene – acrylic ester backbone changes the situation. The resin becomes reactive in addition to be polar while staying easily processable even at high temperature. These terpolymers (brandname Lotader) are made by high pressure process in autoclave reactor, like coating grades of LDPE. As a consequence, they have the typical long chain branching of LDPE, with a high molecular weight fraction ensuring the rheological properties required by the extrusion coating technology, like low neck-in, melt stability and drawability. The acrylate comonomer allows to control polarity, crystallinity and crystallinity related physical properties like elastic modulus, yield strength and melting point. Maleic anhydride brings reactivity with many different chemical groups like hydroxyls and other oxygenated functions. Highly compatible with polyethylene, these terpolymers are processed like LDPE: similar power consumption, same limit in processing temperature, no corrosion.

ADHESIVE PROPERTIES

Inserting two kinds of comonomers inside an ethylenic backbone leads to a very interesting versatility in adhesion, i.e. to the possibility of bonding many different kinds of surfaces.
Two main uses of such terpolymers take advantage of this highly polyvalent reactivity.
- As concentrates for LDPE, these E-AE-MAH terpolymers allow to enhance the adhesion of LDPE to aluminium and to primed films. They introduce some complementary reactivity in addition to the oxidation mechanism developed during high temperature processing of LDPE. Typical content of terpolymer is around 25%.
- As ready-to-use adhesives for many kinds of polar, non polar, fibrous or not, organic or metallic films and foils, the maleic anhydride comonomer reacting with many chemical species, particularly those created by corona treatment of plastic films. The acrylate comonomer has two beneficial effects. It delays crystallisation for longer reaction time, which is useful in such a thermally controlled process. It is also involved in some high temperature chemical mechanisms for bonding.

NEW DEVELOPMENTS FOR MORE VERSATILITY IN ADHESION

Recent advances in terpolymers design, including both comonomers selection and polymerization process, allow to introduce new terpolymers from the same chemistry, with improved adhesive performance, and removal of moisture sensitivity of pellets. Optimized for extrusion lamination, these new terpolymers are proposed as ready-to-use resins. Their rheological properties give a very stable and drawable melt. The problem of sticking to chill and nip rolls in case of overcoating has been solved, even for processing temperatures as high as 325°C (620°F).

The typical field of interest is the extrusion lamination without primer of difficult substrates, together or combined with easier ones like paper, polyethylene films and aluminium foil. Difficult substrates are for instance:
- Oriented plastic films like oPET, oPA, oPP,
- Cast films of PP, PA,
- PVDC coated films, PVC films,
- Special surfaces like some hydrophobic/oleophobic papers,
- Reverse printed films with different ink systems,
- Molten PA or EVOH, in case of coextrusion coating with such barrier resins.

Corona treatment of substrates has very often a positive effect on bonding, creating some oxygenated functions for more reactions with the tie layer of E-AE-MAH terpolymer. For some reverse printed films, better results are however achieved without corona treatment.

THE NOT SO EASY FAQ : HOW STRONG DOES IT STICK ?

This part is more general and deals with the question of peel strength measurements. More precisely, its purpose is to show that peel strength values are strongly dependant on the whole construction of the multilayer being evaluated. Some simple experiments involving an aluminium foil, an adhesive, and varying the thickness of some additional layers allow to discuss peel strength values ranging from 1 to 9 N/15 mm while the interface strength is absolutely the same. If bonding starts with some chemistry at the interface, the physical nature of peel strength is rather plasticity, and some fracture mechanics arguments are to be considered as well.

CONCLUSION

To broaden its possibilities, extrusion lamination is needing versatile adhesives, flexible in processing and easy to purge. The chemistry of Ethylene – Acrylic Ester – Maleic Anhydride terpolymers made by high pressure process in autoclave reactor brings an interesting answer to this request. Highly compatible with LDPE, polar and reactive, such terpolymers exhibit really versatile adhesive properties, which allows to bond many plastic films without primers using extrusion lamination.

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Ultra Versatile Adhesives to broaden the possibilities of Extrusion Lamination

Aim of the presentation

- To discuss why adhesives can be the bottleneck of extrusion lamination development.
- To present new possibilities offered by Ethylene – Acrylic ester – Maleic Anhydride terpolymers.
- To throw some light on the question: How strong does it stick?

Extrusion Lamination: an attractive technology

- High productivity
- Sophisticated structures in one run
- High quality
- Environment friendly (limited VOC)
- No drying step
- No curing time to wait for
- High cost efficiency for large productions
...with however some limitations

- More suitable for long runs than for frequent changes
- Time to reach steady running conditions
- Purging difficulties with many specialty resins
- Time for transitions between uncompatible resins, time for temperature changes, etc
- Lack of versatile adhesives, flexible in processing, safe regarding corrosion and cross-linking risks, and easy to purge

Typical resins used as adhesives

- **LDPE**
  ++ / Processability
  -- / Limited adhesive possibilities

- **E-VA vinyl acetate copolymers**
  ++ / Polar copolymer
  -- / Low processing temperature only
  -- / Limited adhesive possibilities

- **E-VA-acid or anhydride terpolymers**
  ++ / Polar and reactive
  -- / As limited as EVA in temperature

- **E-AA or E-MAA acrylic acid copolymers**
  ++ / Very good adhesion to foil
  -- / Processing risks at high T°, purging
  -- / No adhesion to plastic films

- **E-MA, -BA, -EA acrylic ester copolymers**
  ++ / Processable at high temp.
  -- / Limited adhesive possibilities

What about E-AE-MAH Terpolymers ?

**Ethylene – Acrylic Ester – Maleic Anhydride**

```
  |- (CH2 \- CH2 \-)x
  \- (CH2 \- CH - CH2 \-)y
  \- (CH2 \- CH - CH2 \-)z
  \- (CH2 \- CH - CH2 \-)t
  \- C = O
  \- O = C
  \- C = O
  \- O
  \- R
```

- Random ethylene terpolymers made by high pressure radical polymerization in autoclave reactor.
- Trademark Lotader®.
Chemical structure

Ethylene – Acrylic Ester – Maleic Anhydride

LDPE family

Polarity
Crystallinity control

Reactivity

Autoclave reactor: the suitable choice

- All LDPE used in extrusion coating are « Autoclave resins »
- Why? What difference vs. « Tubular resins »?

- Molecular weight distribution includes a typical high mass fraction, decisive for molten state properties: higher melt elasticity, longer relaxation times
  => Lower neck-in in extrusion coating
  => Excellent melt stability, including edges stability

Processing E–AE–MAH terpolymers

- Basically like LDPE!
  => similar power consumption
  => no corrosion
  => same high limit in temperature (325°C ~ 620 °F)

- Highly compatible with LDPE
  => blendable in all proportions
  => easy purging (incorporation effect)
  => short transitions in production
Adhesive properties

- Very high versatility = ability to stick to many different substrates
- First use: as concentrates for LDPE, these terpolymers are used to improve LDPE adhesion to foil and make it reliable
  - 20% terpolymer improves by 50% LDPE adhesion achieved at high processing temperature by oxidation
  - Interest: very short transitions from or to LDPE, same high processing temperature
- Second use: versatile adhesive for all kind of polar, non-polar, fibrous or not, organic or metallic films and foils
  - Terpolymers used pure mainly,
  - Higher performances with high comonomer content grades

Basic rules to select and use the right terpolymer

- The more difficult the substrate (regarding adhesion), the “softer” the terpolymer to be chosen, i.e. with higher comonomer content

<table>
<thead>
<tr>
<th>Easy</th>
<th>Difficult</th>
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<tbody>
<tr>
<td>Paper</td>
<td>PE</td>
</tr>
<tr>
<td>Board</td>
<td>Ethylene copolymers</td>
</tr>
<tr>
<td></td>
<td>Alu foils</td>
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<tr>
<td></td>
<td>Metallized films</td>
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<tr>
<td></td>
<td>Primed films</td>
</tr>
<tr>
<td></td>
<td>Primerless plastic films</td>
</tr>
<tr>
<td></td>
<td>oPET, oPP, cPP, cPA</td>
</tr>
<tr>
<td></td>
<td>Inks, special surfaces, etc</td>
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</tbody>
</table>

- Adhesion increases with increasing processing temperature, with a transition around 310°C for profitable oxidation and pyrolytic reactions
- Blending in LDPE allows to modulate performance/cost ratio. High blending requires oxidation as additional adhesion mechanism

Any limitation with E-AE-MAH terpolymers?

Of course, a few ones:
- Organoleptics: acrylate smell can be a problem, especially with high comonomer content grades
- Adhesive performance of LDPE blended terpolymers remains limited
- Performance/cost ratio of high comonomer content grades is not always acceptable by flexible packaging markets
- Moisture sensitivity of pellets: MAH hydrolyses, and then water is released during extrusion => terpolymers must be handled like hygroscopic polymers
So, what's new?

- Advances in terpolymers design for adhesive purpose
  - Comonomers selection / Content optimization
  - Manufacturing in high pressure autoclave process
- Performance in adhesion, high versatility
- Elimination of moisture sensitivity
- Reduction of smell level
- Ease of processing, without corrosion or cross-linking
- Optimized for extrusion lamination, these new terpolymers are proposed as ready for use resins, in addition to standard terpolymers usable as concentrates.

More and more versatility in adhesion

<table>
<thead>
<tr>
<th>Terpolymers</th>
<th>Concentrates for LDPE</th>
<th>Ready for use resins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low com.</td>
<td>High com.</td>
</tr>
<tr>
<td></td>
<td>Std Butyl acryl. Methyl acryl.</td>
<td>Std 4403 4503</td>
</tr>
<tr>
<td>MI 5 or 10</td>
<td>MI 5</td>
<td>MI 5</td>
</tr>
</tbody>
</table>

Adhesion level:
- - Not recommended
- Fair
- Good
- Very good
- Excellent

Example 1: Adhesion to OPET films

- Effect of processing temperature on peel strength of new high comonomer content terpolymers on Corona treated OPET
- Structure: OPET 12µm / E-4E-MAH 10µm / LDPE 25µm

Graph showing the effect of temperature on peel strength.
Example 2: Adhesion to OPA films

- Effect of processing temperature on peel strength of new high comonomer content terpolymers on Corona treated OPA
  Structure: OPA 25µm / E-AE-MAH 10µm / LDPE 85µm

Example 3: Adhesion to foil in thick structures

- Effect of processing temperature on peel strength of different terpolymers on soft aluminium foil
  Structure: Alu 37µm / E-AE-MAH 15µm / LDPE 15µm / PE film 100 µm

Example 4: Adhesion to OPET with white MB

- White, bright and strong OPET / foil lamination can be achieved using E-AE-MAH terpolymer + 20% white MB
  Structure: OPET 25µm / Tarpo + 20% White MB 10µm / LDPE 25µm
The not so easy FAQ about adhesives

How strong does it stick?
A few simple experiments to throw some light on peel strength measurements

The not so easy FAQ : How strong does it stick?

- Not so easy to answer in one word!
- Very simple experiments: take a 37 µm thick foil
- Extrude a 10 µm monolayer of adhesive
- Measure T-Peel strength

How strong does it stick? Simple experiments

- 2nd experiment: still onto 37 µm thick foil
- Coextrude 10 µm adhesive + 5 µm LDPE
- Measure T-Peel strength
How strong does it stick? Simple experiments

- 3rd experiment: still onto 37 µm thick foil
- Coextrude 10 µm adhesive + 15 µm LDPE
- Measure T-Peel strength

Peel strength results

- Et cetera, still onto 37 µm thick foil
- Coextrude 10 µm adhesive + up to 100 µm LDPE
  (Can be done either by coextrusion or by coextrusion tie + LDPE + LDPE film)
- Measure T-Peel strength

![Graph showing peel strength results vs. LDPE thickness](image-url)
Why such results?

From adhesion to peel strength

Very different peeling geometries
Different geometries: consequences

Geometry 1

Interface toughness is quite dependant on stress distribution at the crack tip: opening vs shear components

Geometry 2

- Peel strength is dominated by plasticity in peeling arm, and not very sensitive to interface strength.
  => More representative of extrusion coating structures.
- More critical regarding interface strength.
  => More representative of extrusion lamination structures.
- A good adhesive for extrusion coating is not necessarily a good adhesive for extrusion lamination, and vice versa.
- Playing on comonomers type and content, E-AE-MAH chemistry allows to design high performance adhesives suitable for multilayers typically made by lamination.
Conclusions

- Extrusion lamination is needing versatile adhesives, flexible in processing and easy to purge.
- Typical structures made by this technology combine stiff films and foils, situation which requires specific adhesives.
- Ethylene - Acrylic Ester - Maleic Anhydride terpolymers offer wide possibilities in this field, playing separately on polar and reactive monomers.
- In addition to standard terpolymers often used in blends with LDPE, new ready for use grades are today broadening the possibilities of this technology.

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Thank You

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