PRODUCT APPLICATION NOTE

Tie layer adhesive polymer for multi-layer films

PLUSS-DOC-783 Version no.-R01, July-2024

PLUSS® TECHNOLOGY FOR A BETTER WORLD

CUMI

Introduction

Packaging films play the dual role as an attractive container for products, as well as preserving the contents until use. In the latter role, packaging is supposed to have adequate mechanical and barrier properties to retain product integrity as well as shelf life during transit and storage. From performance and cost considerations, multiple materials may be required to be used in multilayer structures, to meet diverse requirements like mechanical strength, printability and barrier to moisture, oxygen, odour etc.; runnability on FFS machine, heat sealability and so on. Most of the time, such properties come from chemically dissimilar materials such as paper or aluminum foil or speciality polymers like nylon, polyester or EVOH, combined with commodity polymers such as polyethylene and polypropylene.

Multilayer film structures made by lamination of the different substrates, using solvent-based or solvent-less adhesives, is a well-established practice in trade. However, co-extrusion of multiple polymers into a multilayer film (MLF) in a single operation has revolutionized flexible packaging application. Some of the obvious advantages of co-extruded multilayer films over similar laminated structures are given in the table below.

#	Characteristics	Laminated MLF	Co-ex MLF
1.	Production time	Long- Individual Films to be made first and then laminated, sometimes in multiple passes.	A single operation.
2.	Production wastage	More waste due to multi stages operations	Less waste due to single operation
3.	Product manufacturing cost	Higher cost of making each substrate, each lamination step involves wastage of film and adhesives adding to overall product cost	Lower processing cost. However, capital cost is higher.
4.	Optimum material usage	Unable to use thin individual layers due to manufacturing and handling limitations.	Thin layers possible
5.	VOC concerns	Solvent based adhesives can render the film unsuitable for food packaging	Not a concern.

Co-extruded multilayer films can be made in both blown and cast varieties in oriented or non-oriented versions. To be able to combine chemically different materials in all the mentioned structures, we need to use a tie layer in-between.

BindEX E-189 AS TIE LAYER

Starting with minimum of 5-layers, structures with higher number of layers are made using 3 or more extruders. Higher number of layers affords flexibility of using materials more economically for a given set of mechanical and barrier properties.

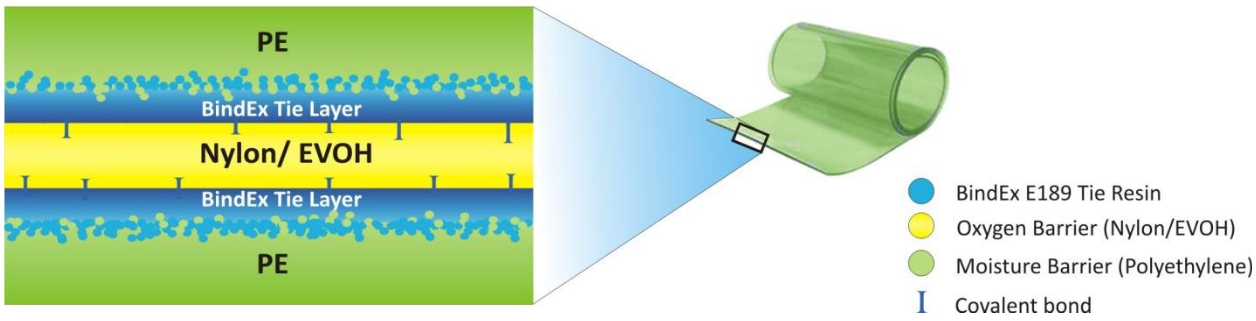

Fig. 1: Schematic Diagram of multilayer coextruded film of Nylon and Polyethylene using BindEX tie layer resin.

BindEX E-189 is a maleic anhydride grafted polyethylene adhesive resin from Pluss. It is the recommended tie layer material for making multilayer films in conventional co-extrusion equipment. It has suitable pendant functional groups to bond to polar polymer layer on one side, while its polyethylene backbone has natural affinity with the non-polar polyolefinic layer on its other side in the multilayer structure. BindEX E-189 can be used to combine Nylon 6, Nylon 66, and EVOH for gas barrier properties with variety of HDPE, LLDPE, LDPE & PP grades for different functions like sealability, moisture barrier and providing bulk to the structure. It can be used in its pure form as well as in diluted form, depending on the degree of inter-layer adhesion required in the end-application. Dilution level can vary from 50-80% with a polyolefin compatible with the adjacent polyolefin layer in the multilayer structure.

Tie layer Mechanism

Tie layer material is co-extruded as to lie between polar barrier nylon or EVOH and non-polar polyolefin material. Maleic anhydride groups present in BindEX chemically react with amine groups of nylon or hydroxyl groups of EVOH at processing temperatures, on one side, while polyethylene part of BindEX adheres naturally with polyethylene on the other side, thus giving a composite structure. At processing temperature, strong adhesion between tie layer molecules and the barrier polymer molecules results, due to formation of covalent bonds between the anhydride functional group on tie layer resin and hydroxyls (-OH) or amine ($-NH_2$) functional groups of EVOH or nylon barrier layer, as shown in the diagram below.

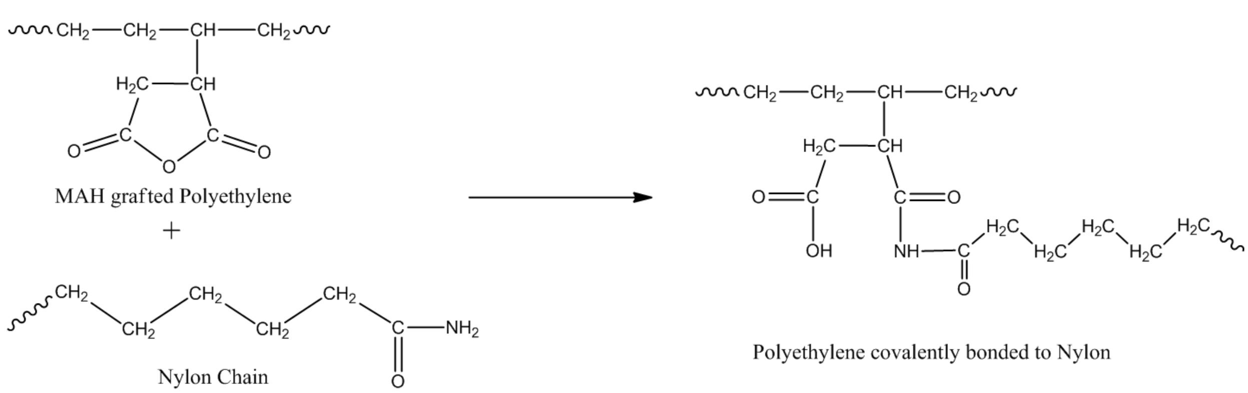

Fig. 2: Reaction of Maleic Anhydride grafted Polyethylene with Nylon

On the other side, polyolefin backbone chains in BindEX E-189 can diffuse into compatible polyolefin chains of the moisture barrier or sealant layer and form strong bond due to chain entanglement, as the two layers co-crystallize in cooling.
For chain entanglement to occur, the adjacent materials must be in the melt state, be physically and chemically compatible and have sufficient contact time. Diffusability of the materials is related to the wetability of the materials. If the resins have similar surface energies and are compatible, the resins are considered to have good wettability. The polar functional groups in tie layer resin facilitate its wetting of the barrier layer.

Factors affecting inter-layer adhesion

T- peel adhesion strength is generally measured as g/25mm width of the film sample. Inter-layer adhesion strength in a coextruded multilayer structure depends on various factors such as:

1. Proportion of reactive functional groups in tie layer composition.

2. Tie layer thickness: Higher tie layer thickness yields higher adhesion strength up to a limit and then it levels off.

3. Processing conditions: Adhesion is clearly a factor of processing temperature during film making. Depending on the barrier polymer used, the temperature can be high or low. Reaction between anhydride functional groups on tie layer resin and amino or hydroxyl groups of nylon or EVOH barrier layer, is faster at higher temperature. Inter-layer adhesion can be increased by increased melt and die temp, due to enhanced rate of chemical reaction and rate of diffusion leading to chain entanglement. However, temperature is limited by polymer degradation which may otherwise cause gel formation, colour, black specks or loss of mechanical properties.

4. Storage Conditions after film production: Adhesion strength after co-extrusion initially increases with time, then levels off. It may deteriorate over a period, depending on storage conditions, among other factors. Exposure to heat and significant levels of moisture have particularly detrimental effect. It is recommended that T- peel adhesion strength is measured only 72 hours after extrusion.

5. In adhesion test, the site of failure should be observed carefully. Sometimes the barrier resin may fail during testing cohesive failure, rather than the adhesive bond.

Optimizing performance-to-cost ratio

While we may want maximum adhesion in a multilayer structure, it would mean using a thicker tie-layer or a resin with higher proportion of reactive chemical groups. Both these options tend to increase costs. The preferred approach then is to figure out the minimum adhesion required for the given application environment and choose layer thickness as well as dilution level. Safety margin should be added to account for machine inconsistency in maintaining tie-layer thickness variation.

Processing guidelines:

Tie layer resin can be processed on most of the standard extrusion equipment designed to process conventional polyolefins. Maximum processing temperature should not exceed 280°C. In case of shutdown, care should be taken to leave extruder filled with polymer other than BindEX; otherwise, gels may appear in subsequent production.

For the tie layer extruder shutdown, the best practice is to use one of the polyolefin components of the film under production. In case of short duration stoppage, ideally the extruder should be kept running at minimum possible throughput to avoid generation of gels.
Extrusion temperatures for tie layer resin are typically kept between 195-215^{0}C.

A typical case study

Machine type: Windsor-Kuhne make 5-extruder, 5-layer coextruded blown film plant
Total Film Thickness: 100 - 105 µm.
Output: 200 Kg/hr.
Film Structure: PE (41µm)/Tie resin (5µm)/Nylon-6 (8µm)/Tie resin (5µm)/PE (41µm)

Materials Used

i. PE used in outer and inner layers was film extrusion grade (MFI: 1.0 g/10min @ 190 °C/2.16 Kg),
ii. Nylon-6 used was film extrusion grade Ultramid B40L from BASF
iii. Tie resin was BindEX E-189 diluted with 80% Sabic LLD 118 NJ

Composition

LAYER →	**Outer Layer (PE)**	**Tie Layer** BindEX E-189 + **Sabic LLD 118 NJ (20 : 80)**	**Barrier Layer (Nylon 6)**	**Tie layer** BindEX E-189 + **Sabic LLD 118 NJ (20:80)**	**Inner Layer (PE)**
Thickness (µ m)	41 – 42	5 – 6	8 – 9	5 – 6	41 – 42
Screw RPM	93	29	31	29	93

Film Properties

Depending upon the end application of the film, different properties can be tested. Film made in this case study goes for oil packaging. Properties of major importance are film surface, tackiness, waviness, gels, un-molten particles, tensile strength, elongation, heat seal strength and dart impact strength.

S. No.	Film Properties	Unit	Testing Method	Observations
1.	Surface appearance	NA	Visual	No surface defect observed
2.	Tackiness	NA	Manual	No tackiness observed
3.	Gels	NA	Visual	No disruptive gels
4.	Inter Layer adhesion	Kg/25mm	Pluss Method	Layers can't be separated.
5.	Tensile Strength at Break MD/TD	MPa	ASTM D882	25.8/19.8
6.	Elongation at Break MD/TD	MPa	ASTM D882	570 / 545
7.	Dart Impact Strength	Gram	ASTM D1709	390

Availability

The following products are available with different MAH percentage, melt indices, base polymer and concentrated or diluted form:

- BindEX E-187
- BindEX E-188
- BindEX E-189
- BindEX P-187

Tie layer resin is a regular grade of Pluss Advanced Technologies, manufactured at our plant at Bawal, in the state of Haryana, India. BindEX speciality polymers are supplied in pre-dried form in 25 Kg (55 lbs) PE lined, HD woven cloth laminated paper bags and 750 Kg (1653 lbs) FIBC's. Depending upon the customer's requirement, the bags can be further palletized for dispatch. They should be stored in a cool and dry place.