



# *An Introduction to* **PLEXAR®** **TIE LAYER RESINS**



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## AN INTRODUCTION TO PLEXAR® TIE-LAYER RESINS

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### ABSTRACT

Extrudable adhesives are used in coextrusion and lamination to bond two dissimilar materials together that otherwise would have poor adhesion to each other. The use of reactive systems, namely anhydride-modified polyolefins, in coextruded multilayer applications is discussed. The reasons behind how extrudable adhesives work are given along with a review of various adhesion mechanisms. The factors that affect adhesion during coextrusion are reviewed including processing and resin parameters. The information needed and the process of selecting an extrudable adhesive are covered. Guidelines for handling and processing extrudable adhesives are provided.

### INTRODUCTION

Plexar tie-layer resins are chemically-modified polyolefins used as extrudable adhesives in coextrusion or coating operations to bond two dissimilar materials together that otherwise would have poor adhesion to each other. As a result, multilayer structures with unique properties can be produced that combine key properties of each type of material. For example, polyolefins such as high-density polyethylene (HDPE) have poor adhesion to ethylene vinyl alcohol copolymers (EVOH). By using Plexar resins, a product combining the properties of EVOH (low oxygen permeability) and HDPE (stiffness) can be created. Plexar resins can be used in a variety of applications, such as extrusion coating, blown and cast film, blow molding, extrusion lamination, sheet, thermoforming and other specialty processes.

Various tie-layer resins can be used depending on the materials to be bonded and the amount of adhesion required. Tie-layer resins can either be reactive or non-reactive. Non-reactive extrudable adhesives include polar resins such as ethylene vinyl acetate (EVA) and ethylene methyl acrylate (EMA). Acid-modified resins are generally considered non-reactive but can provide good adhesion in some applications due to hydrogen bonding and polarity. Anhydride-modified polyolefins (AMP) are the most commonly used tie-layer resins for coextrusion since they are capable of chemically reacting with materials such as nylon, paper, some metals and EVOH to provide excellent adhesion. AMP are also being used with resins such as polyethylene terephthalate (PET) or polyvinylidene chloride (PVdC) where the increased polarity compared to unmodified polyolefins can result in improved adhesion. This paper focuses on AMP and provides guidelines on how to best use tie-layer resins in multilayer applications.

## DISCUSSION

### Factors Affecting Adhesion in Coextrusion

Table 1 shows a schematic of how various process variables affect adhesion. For a given tie-layer, increasing the contact time usually increases adhesion since there is a longer time for the chemical reaction and chain entanglement to occur. Contact time is affected by processing variables such as chill roll temperatures, line speed and die design.

**Table 1. The effect on adhesion strength by increasing the given variable**

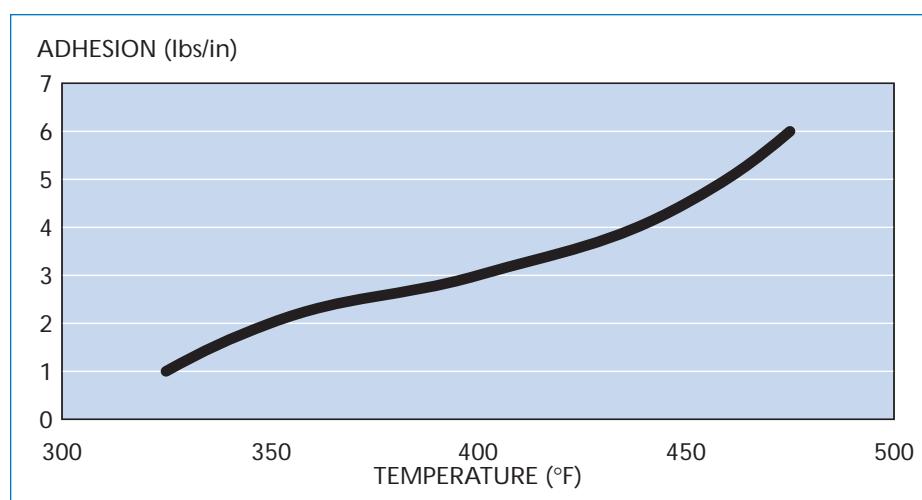
Adhesion increases with an increase in:	Adhesion decreases with an increase in:
Tie-layer thickness	Orientation
Contact time	Line speed
Functionality	Thermoforming draw ratio
Melt temperature	Blown film blow-up ratio

The application process can also affect adhesion. High interfacial stress can lead to lower adhesion. Orientation during or after processing (e.g., thermoforming) increases interfacial stress and also reduces the number of reaction sites per unit area, usually leading to a decrease in adhesion.

Properties of the tie-resin, such as shrinkage, physical properties and graft levels, are also important. If one layer in a structure has high shrinkage compared to the other layers, interfacial stress can reduce adhesion or the film may curl.

Higher melt and die temperatures generally improve adhesion since the rate of reaction and diffusion (i.e., chain entanglement) is accelerated. Figure 1 shows that increasing the heat-seal temperature increases the adhesion strength of modified EVA to nylon 6. While higher temperatures generally improve adhesion, it is important not to exceed the recommended processing temperatures due to potential processing problems, gel formation or even resin degradation. EVA resins are more sensitive to degradation compared to other polyolefins. AMP tie-layers

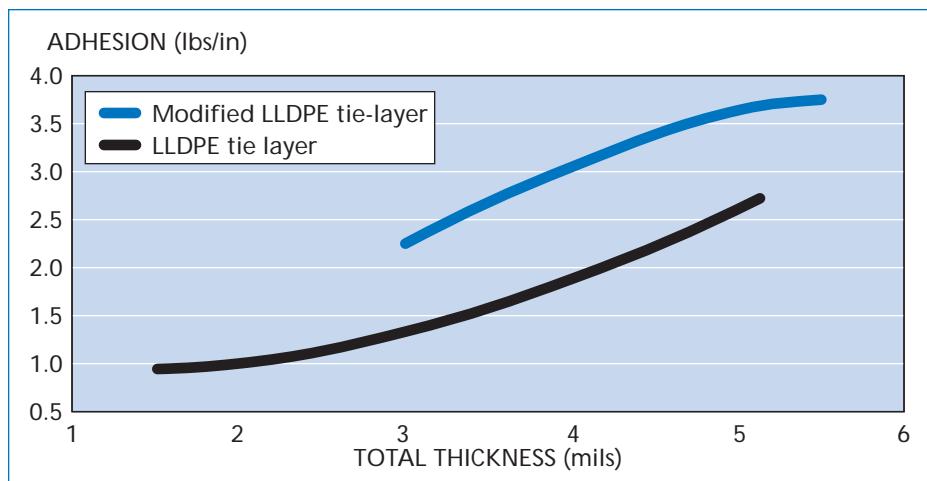
**Figure 1. Lamination of 9% EVA tie-layer to nylon-6 at various temperatures**



are typically processed at 400-450°F but non-EVA tie-layers can be processed as high as 620°F under controlled conditions. Thermal stability of the tie-layer will depend on both time and temperature in the extruder.

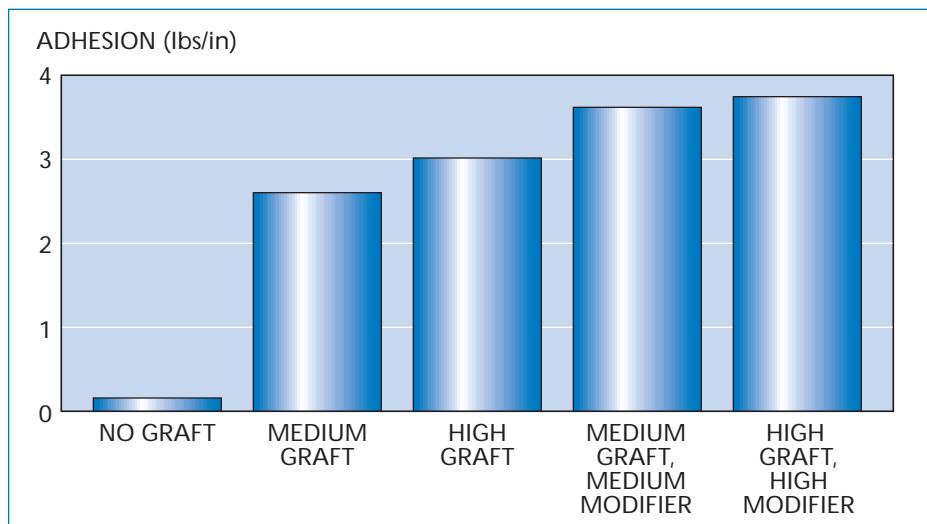
The thickness of the tie-layer also affects adhesion. Increasing the thickness of the tie-layer, which increases the level of reactive sites and amount of material available to absorb energy, generally increases adhesion up to a plateau value. Figure 2 shows the beginning of the plateau region for a modified LLDPE tie-layer. At a critical point, adhesion increases rapidly as a function of thickness as shown for a LLDPE tie-layer. Therefore, not using enough tie-layer could result in adhesion failures. It is critical to test products under the most extreme conditions including potential variations in processing temperature or tie-layer thickness.

**Figure 2. Effect of total film thickness on adhesion for a coextruded, cast film with a structure of HDPE/tie/EVOH/tie/HDPE and a layer distribution of 36/8/12/8/36 for two LLDPE tie-layers**



The properties of the resin will also affect adhesion. Figure 3 shows the adhesion strength of various LLDPE tie-layer resins in a cast film structure of HDPE/tie/EVOH/tie/HDPE. This difference in adhesion performance between these LLDPE tie-layer resins can be attributed to the overall physical properties of the resin and the level of functionality. The physical properties of the resin can be enhanced with modifiers and the functionality can be adjusted for the application. Again, the application process can also affect adhesion.

**Figure 3. Adhesion of various LLDPE tie-layers in five mil cast film with a structure of HDPE/tie/EVOH/tie/HDPE and a layer distribution of 36/8/12/8/36**



### **How Reactive Tie-layers Work**

Understanding various adhesion mechanisms is important to understanding why good adhesion is achieved with certain materials but not with others. Adhesion between two polymer substrates can occur by a variety of mechanisms. In decreasing order of typical adhesion strength, the various adhesion mechanisms are:

- Chain entanglement
- Covalent bonding
- Hydrogen bonding
- Dipole-dipole non-hydrogen bonding
- Van der Waals forces

Covalent bonds are formed by the reaction of two chemical groups and typically result in the highest adhesion. Covalent bonds typically provide excellent adhesion since they require significant energy to break. In AMP, covalent bonds can result from the reaction that occurs between the functional group in the tie-layer and the bonding substrate. Anhydrides will react with groups that contain labile hydrogen, such as hydroxyls ( $\text{OH}$ ) and amines ( $\text{NH}_2$ ), but otherwise do not typically form a covalent bond. For example, the anhydride group in the AMP will react with the hydroxyl group in the EVOH to form an ester linkage, but AMP will not react with the side-chain aromatic group on polystyrene.

Besides covalent bonding, the other kinds of chemical bonding are dipole-dipole interactions and van der Waals forces. Dipole-dipole interactions occur when the positive end of one polar molecule is attracted to the negative end of another polar group. Conversely, two identical atoms bonded together are non-polar as with polyethylene. The C-H bond has very limited polarity which does not result in dipolar bonding. An especially strong kind of dipole-dipole attraction is hydrogen bonding. The positively charged hydrogen is attracted to, but does not react with, a negatively charged functional group. To have a sufficient positive charge for hydrogen bonding, the hydrogen atom must be connected to an electronegative atom such as nitrogen or oxygen. Acids ( $\text{COOH}$ ), amines ( $\text{NH}_2$ ), amides ( $\text{NHCO}$ ) and hydroxyls ( $\text{OH}$ ) groups can therefore have hydrogen bonding, while a methyl group is essentially non-polar and is not capable of hydrogen bonding. The strength of the hydroxyl hydrogen bond ( $\text{H}\dots\text{O-H}$ ) is about one tenth that of the hydroxyl ( $\text{O-H}$ ) covalent bond. An even weaker interaction, but still important factor, is van der Waals forces. These forces result from the small dipoles that exist in all molecules and require that the polymer chains be in very close proximity to have an effect.

While chemical interactions are important for bonding, resins such as low-density polyethylene (LDPE) and EVA typically have excellent adhesion to each other although no covalent bonding or dipole-dipole interaction occurs. These materials adhere well due to chain entanglement whereby polymer chains diffuse into the other material and become entangled. If the materials are semi-crystalline, co-crystallization can occur which further improves adhesion compared to chain entanglement in the amorphous state. In order for chain entanglement to occur, the materials must be in the melt state, be compatible and have sufficient contact time. The ability of the materials to diffuse is related to the wettability of the materials. If the resins have similar surface energies and are compatible, the resins are considered to have good wettability. Table 2 shows examples of polymer substrates and the adhesion mechanisms that are present.

In summary, tie-layers achieve adhesion through a variety of mechanisms. In a typical structure with a polyolefin and a polar substrate, the tie-resin must be compatible with the polyolefin but chemically interact with the polar substrate by either reacting to form a covalent bond, which is preferred, or by having sufficient polar interactions.

**Table 2. Adhesion mechanisms when bonding substrates**

Substrate 1	Substrate 2	Typical adhesion	Covalent bonding	Hydrogen bonding	Dipole-dipole non-hydrogen bonding	Van der Waals	Chain entanglement
EVOH	Plexar	Excellent	•	•	•	•	•
EVOH	Nylon	Good		•	•	•	
EVOH	HDPE	Poor				•	
Nylon	Plexar	Excellent	•	•	•	•	•
Nylon	EVA	Fair			•	•	
Nylon	Ionomer	Fair			•	•	
Nylon	Acid copolymer	Good		•	•	•	
Ionomer	EVA	Fair			•	•	
PS	EVA	Fair			•	•	
EVA	PET	Fair			•	•	
Aluminum	Plexar	Excellent	•	•	•	•	•
EVA	LDPE	Excellent				•	•

### **Adhesion Testing Methods**

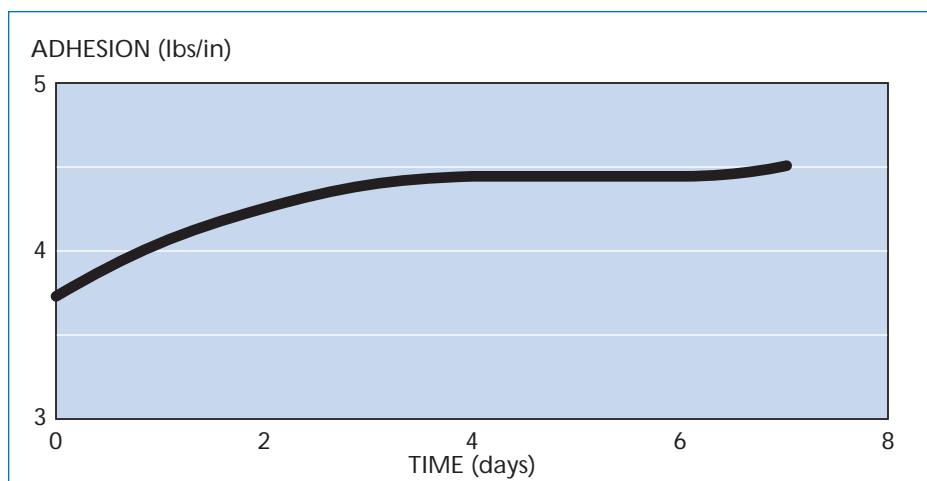
Adhesion is reported as the force required to separate a sample per specimen width. Conversions for different reported adhesion units are shown in Table 3. The typical width of strips is one inch. If adhesion is high, strips with a one-half inch width can be used. Variables for adhesion testing include testing speed, configuration, aging time, structure, and size of sample. It is important that results only be compared for samples with one variable change unless a designed multivariable experiment is being performed.

Figure 4 shows the adhesion after several days. Adhesion initially increases as a function of time. Therefore, it is important to compare samples that have been

**Table 3. Unit conversions for adhesion testing**

1 lb/in	=	4.45 N/25.4 mm
	=	268 g/15 mm
	=	0.175 N/mm
	=	179 g/cm

**Figure 4. Adhesion strength as a function of time for a five-layer film of HDPE/tie/EVOH/tie/HDPE**



aged for the same amount of time. Samples can be initiated right away but it is recommended to wait at least 72 hours before determining adhesion strength.

### **How to Select a Tie-layer**

Table 4 lists the information needed to select and evaluate a tie-layer resin. The tie-resin should be selected based on the resins being bonded. For example, an AMP tie-resin is going to provide minimal benefit for adhering polyolefins to each other. Also, a tie-resin that performs well for one substrate may or may not perform well with a different substrate. The processing conditions, any secondary operations (e.g., orientation or thermoforming) and the end-use environment will all effect the performance of the tie-resin. It is imperative that the conditions most likely to cause adhesion failures are identified. These conditions may occur during retort, orientation during processing, at a point of high stress in a thermoformed part or during use by the consumer.

**Table 4. Information that is needed to select the proper tie-layer resin**

• Adhesion strength	• Economics	• Conversion method(s)
• Substrates to be bonded	• End-use requirements	• Process parameters
• Physical requirements	• Optical requirements	• Regulatory requirements

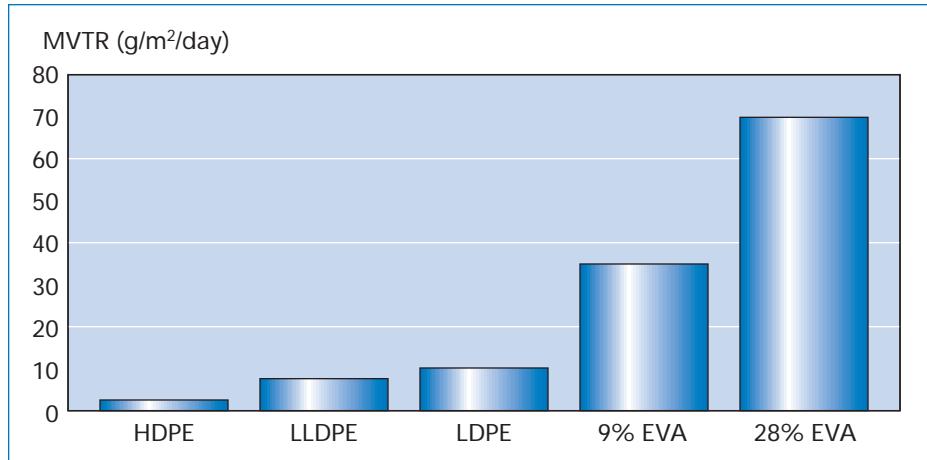
Processors often desire maximum adhesion in their multilayer structure, however, maximum adhesion means using a thicker tie-layer or a higher performance resin which are both costly alternatives. Therefore, the minimum adhesion should be determined by measuring adhesion under the most severe conditions and including a safety factor. This information can then be used to select the most cost-effective tie-resin and layer thickness. Any regulatory requirements, such as those of the Food and Drug Administration (FDA), must also be identified. The performance requirements other than adhesion should also be considered. The tie-resin, which is often thought of as simply an adhesive, can effect machinability, clarity and physical properties, such as puncture, stiffness and moisture vapor transmission rate (MVTR).

Once this information has been collected, the proper Plexar resin can be identified based on the resin type, melt index and cost. A grafted resin will have similar properties as the resin backbone, which can be useful in selecting a resin type. Key properties for polyolefins are shown in Table 5. For example, a HDPE tie-layer will have higher stiffness and lower MVTR than a comparable EVA but with lower clarity. Figure 5 shows a comparison of MVTR values for various tie-layer resins. HDPE resins have high crystallization that gives good chemical resistance and better thermal resistance than LDPE. However, the high degree of crystallization results in higher shrinkage compared to other polyolefins that can lead to lower adhesion due to high stress at the interface. Therefore, HDPE tie-resins are typically used in combination with HDPE resins. For film applications, LLDPE tie-resins are increasingly popular due to a good combination of physical properties and processability.

**Table 5. Two key characteristics for each type of anhydride modified polyolefin resin**

EVA	Clarity	Polarity for adhesion
LDPE	Processability	Clarity
LLDPE	Elongation	Tensile strength
HDPE	MVTR	Stiffness

**Figure 5. MVTR of various tie-layer resins at 100 percent relative humidity**



The melt index should be selected so that the layers in contact have similar viscosities; otherwise, flow instabilities can lead to waviness or poor layer distribution. Furthermore, the interior layer should have the highest viscosity, while the skin layer should have the lowest viscosity. Simply matching the melt index may not always be sufficient but is a good starting point. For example, EVOH is not as shear thinning at PE, so at high shear rates it would be necessary to use resins with a different melt index.

*Example:* Cast film was being produced with the following structure: LDPE/tie/EVOH/tie/EVA and melt indices: 6/2/4/2/6. A flow instability was seen as nonuniform layer distribution and parabolic flow lines. By changing the melt index of the EVOH from 4 g/10 min to 2.4 g/10 min, the cast film quality was greatly improved.

A tie-resin should be selected that gives the overall best value to the processor. The processor who selects a tie-resin simply based on the lowest cost resin may be missing cost savings by not downgauging a higher performing, but more expensive, tie-resin or may not be achieving maximum product performance based on the properties of the tie-resin.

#### ***Handling Guidelines for Tie-layers***

AMP tie-resins should be stored in closed bags and not subjected to high levels of moisture. Drying of AMP tie-resins is generally not required. However, AMP tie-layers can hydrolyze in the presence of moisture resulting in a diacid that is not as reactive as the anhydride that could result in lower adhesion. LyondellBasell technical representatives should be consulted for specific recommendations if it is believed that Plexar resin may have been exposed to moisture for an extended time.

#### ***Purging Guidelines***

An improper shutdown can lead to significant gel issues. A shutdown should be done using a resin other than Plexar, such as LDPE. Typically, an extruder should not be allowed to idle more than 30 minutes when containing Plexar resin and even then a small amount of throughput is recommended. Plexar PX 909 is an effective purge for EVOH and nylon but should not be left in an extruder that is idle or will be shut down.

## SUMMARY

Extrudable adhesives can be used in a variety of coextrusion processes to adhere dissimilar materials to produce a number of end-use products with the desired attributes. The selection of the tie-resin is important to the overall performance of the package and the processor should consider all conditions of use and desired properties. The processor who selects a tie-resin simply based on the lowest cost resin that provides good adhesion may be missing cost savings by not downgauging a more expensive tie-resin or not achieving maximum performance based on the properties of the tie-resin. Therefore, it is recommended that processing and performance requirements be reviewed early in the package development process to find the optimal resin for a given application.

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