Optimizing the performance of coextrudable adhesive resins

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Coextrudable adhesives with similar formulations can have widely different peel strengths. Testing under simulated production conditions is a must.

Coextrudable adhesive (CXA) resins are used in a wide range of multilayer constructions. Obtaining adequate adhesion among the extruded layers of a construction can be a highly challenging task. Converters are continually demanding CXA resins that will bond diverse plastics in a cost-effective manner. Suppliers have responded by developing sophisticated CXA formulations that can be quite expensive. Converters thus have a strong incentive to optimize the use of CXA resins to ensure adequate performance and to hold down costs.

Optimization of CXA performance involves three distinct areas of consideration:

- Selection of appropriate resin
- Processing considerations
- Evaluation of performance.

I. Selection criteria and associated performance characteristics for CXA resins

CXA selection criteria	*CXA resin parameters*
Peel strength	Adhesion Tensile properties
Processing	Rheology Thermal stability Melt strength
End-use performance	FDA compliance Water-vapor transmission rate Clarity Oil resistance Toughness Stiffness
Cost	Price

Selecting CXA resins

The first point to consider is whether a CXA resin is required. Many constructions do not need a tie resin. For example, CXA resins are not needed when bonding polypropylene (PP) to ethylene vinyl acetate (EVA) copolymers or nylon to ethylene methacrylic acid (EMAA) copolymers. In many cases, plastic layers can be bonded using resins that are not considered to be traditional CXAs. For example, EVA can be used to bond polyvinylidene chloride (PVDC) to PP, and EMAA (with a low-weight percent of MAA comonomer) can be used to bond ionomer to low-density polyethylene (LDPE).

For films that require a CXA, the choosing of an appropriate resin can be overwhelming. Often, more than one CXA resin will satisfy the requirements of an application, and a converter will have a choice among suppliers and grades of resins. In some cases, only one resin will be satisfactory, and sometimes no resin will satisfy all needs.

During the preliminary stage of the CXA selection process, the converter should determine the optimum performance characteristics needed for a given application before the actual development work begins. The converter identifies the criteria that are important to the success of the development and then matches these requirements with the expected performance of the CXA resin. The criteria of interest to the converter are listed in **Table I**.

The key to the CXA selection process is access to the information needed to make intelligent decisions. In choosing the best CXA resin for a particular application, the converter must rely on his or her own knowledge as well as the experience of the supplier. All suppliers publish a list of their CXA product line, but this list is often simplistic and offers little guidance in selecting one grade over another. The supplier's technical organization should be able to offer advice that will help the user make the proper selection.

DuPont has developed software (Smart Choice®) to help the converter organize the CXA selection process into a rational series of steps. The user specifies a multilayer structure and responds to a series of interactive questions and rating procedures. The computer program then selects the optimum CXA resin for the application. The program also produces a written report and contains basic product data and safety information. The software, along with consultation with our technical organization, simplifies the process of selecting the optimum CXA resin for a given application.

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II. Peel strength of various CXA resins used in multilayer structure*

CXA resin	*Type of resin*	*Peel strength, g/in.*
B-1	LDPE	398
B-2	LDPE	554
L-1	Terpolymer	311
P-1	LDPE	882
P-2	LDPE	848

*LDPE-coated paper substrate - CXA - EVOH - CXA - LDPE

III. Peel strength of various CXA resins used in blown films[a]

CXA resin	*Type of resin*	*Peel strength, g/in.*
	2-mil film (0.5/0.5/1.0)	
B-2	9% VA	817
B-3	18% VA	698
B-4	LDPE	CNS[b]
	4-mil film (1.0/1.0/2.0)	
B-2	9% VA	713
B-5	9% VA	1112
B-6	18% VA	795
B-3	18% VA	708
S-1	Zinc ionomer	50

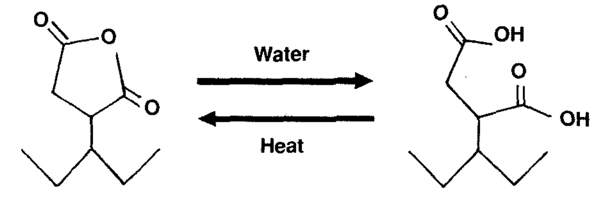
[a]Amorphous polyamide - CXA - zinc ionomer
[b]Could not separate

Once the field has been narrowed down to one or more candidates, evaluation of the CXA resins should proceed under conditions that reflect actual production conditions. CXA resins that appear to be similar in formulation may produce different results. **Table II** shows the results of peel-strength evaluations from an experiment where various CXA resins were used to coextrude both EVOH and LDPE onto LDPE-coated paper. CXA resins B-1, P-1, and P-2 are all rubber-modified LDPE resins containing anhydride functionality. However, the resins do not produce the same results. A third CXA, L-1, with a different formulation, produced yet another result.

Table III shows the same effect in a set of blown-film experiments run more than a year apart from each other. One experiment was run with a 2-mil film, and the other was run with a 4-mil film. In both cases, a variety of CXA resins were used to bond an amorphous polyamide to a zinc ionomer. Table III shows that, with the exception of B-5, all of the EVA-based CXA resins produced about the same level of peel strength, regardless of the level of VA. The LDPE formulation (B-4) produced inseparable bonds, while a zinc ionomer (S-1), the same material used in the seal layer and the same that produces good bonds to nylon 6, produced a very low peel strength.

The need for testing to optimize CXA selection can even be extrapolated to evaluating different substrates. **Table IV** shows the result of an experiment where two different CXA resins were used to bond a polyamide to LDPE. In this experiment, the polyamide was a blend of amorphous polyamide (the same one used in the blown-film experiments described in Table III) and nylon 6 (PA6). With both CXA resins, B-4 and B-7, it is clearly apparent that the peel strength is dependent on the blend ratio. Higher levels of PA6 produce higher peel-strength values. The B-4 adhesive, which is a rubber-modified LDPE, produced higher peel strengths than B-7, which is not rubber modified.

1. Anhydride groups react with moisture to form a diacid. When heat is applied to the diacid, the anhydride is re-formed.



IV. Effect of substrate on peel strength of the CXA resins used in multilayered structures.[a]

PA6/amorphous PA, blend ratio	*Peel strength, g/in.*	
	CXA B-4[b]	*CXA B-7*
0/100	876	383
30/70	1165	...
50/50	1003	...
80/20	1700	1165
100/0	CNS[c]	...

[a]PAG/amorphous PA - CXA - LDPE (layer thickness = 0.8, 0.8, and 1.6 mils, respectively)
[b]Rubber modified
[c]Could not separate

Processing CXA resins

Most CXA resins are chemically-modified polyolefin resins. The procedures for processing these CXA resins are similar to those used for the unmodified polyolefin, with some exceptions that are unique to CXA resins.

Optimization of CXA processing involves proper resin handling, an appropriate temperature strategy, and other techniques. Because most CXA resins are not hygroscopic, they generally do not require drying. However, all CXA resins should be treated as moisture-sensitive materials. Boxes or bags containing unused resin should be tightly resealed for storage. In cases where the projected use of a CXA resin is very large, it would be wise to consider the feasibility of bulk shipping at the beginning of the

V. Effect of chill-roll temperature on peel strength of CXA resin used in multilayered structure*

CXA resin	*Chill-roll temp., °C*	*Peel strength, g/in.*
B-1	21	433
B-1	27	502

*LDPE-coated paper substrate - CXA - EVOH - CXA - LDPE

VIII. Effect of temperature on peel strength of CXA resins used in multilayered thermoformed container*

		Peel strength, g/in.			
		121°C exposure		*134°C exposure*	
CXA resin	*21°C*	*At 121°C*	*After cool down (21°C)*	*At 134°C*	*After cool down (21°C)*
A-3	238	1020	544	850	884
B-12	340	1105	1394	833	1190

*PP - CXA - EVOH - CXA - PP

VI. Effect of CXA layer thickness on peel strength of CXA resin used in multilayered structure*

CXA resin	*Thickness, mils*	*Peel strength, g/in.*
B-1	0.2	260
B-1	0.3	398
B-1	0.6	554

*LDPE-coated paper substrate - CXA - EVOH - CXA - LDPE

VII. Effect of temperature on peel strength of CXA resins used in blown film[a]

	Peel strength, g/in.[b]	
CXA resin	*21°C*	*After 126°C retort*
A-2	1453	1149
B-10	272	695
B-11	2633	1362

[a]Polyamide - CXA - EVOH - CXA - PP
[b]Peel strength was measured at 21°C in both cases.

development stage. Some resins, such as LDPE-based CXAs, can be easily shipped in bulk. Others, based on EVA copolymers with high levels of VA, are not readily bulk shippable. Most suppliers offer a discount for bulk shipment, and cost savings can be significant.

Extrusion temperature is a critical aspect of CXA resin performance. There are the standard considerations (relating to the softness of a CXA resin) that may dictate whether a water-cooled hopper or screw is required to ensure adequate feeding to the extruder. Converters also should avoid exceeding the maximum recommended processing temperature. We generally consider the maximum processing temperature for an EVA-based CXA to be 230°C (460°F). Polyethylene-type CXA resins can be processed at higher temperatures.

Anhydride-containing CXA resins are a special case. Anhydride groups react with moisture to form a diacid, as shown in **Fig. 1.** Conveniently, application of heat to the diacid re-forms the anhydride. The rate at which this conversion from diacid to anhydride occurs is directly affected by the temperature of the resin. Our tests show that the rate of conversion is effectively complete when the resin is exposed to temperatures greater than 200°C (392°F) for several minutes. Since this time frame is generally easy to obtain in normal extrusion processes, optimizing the performance of anhydride-modified CXA resin performance will involve melt temperatures in excess of 200°C in the system. The CXA resin can be exposed to these temperatures in the extruder, piping, feed block, die, or any combination of the above. Exposure to temperatures less than this may also be permissible in systems where the CXA has long residence times. However, there is always the risk that the resin will not have been completely activated.

It is generally best to run the CXA as hot as possible to get the best adhesion. The temperature should be limited by the maximum processing temperature of the CXA and the requirements of other resins in the system. It is common for extrusions with EVOH and other thermally-sensitive materials to be produced with a die with a low temperature setting. In this case, it is not possible to activate the CXA resin in the die. Instead, the CXA can be exposed to temperatures greater than 200°C in the front zone of the extruder and pipes. Using this approach, the die remains cool enough for the thermally-sensitive material.

Of course, an effective temperature strategy also requires the ability to adequately measure and control temperature. *The temperature of the CXA resin should always be* determined by a thermocouple in the melt rather than relying on the set-point temperatures in the extruder zones.

Other parameters also affect the performance of CXA resins. **Table V** shows the influence of chill-roll temperature on peel strength. As can be seen, a higher chill-roll temperature resulted in a higher peel strength. The results in **Table VI** show that a thicker CXA layer resulted in a higher peel strength.

The chill-roll temperature result reflects a general rule that says CXA performance is optimized by keeping the system as hot as possible for as long as possible. Running a process under conditions where heat is removed too quickly can reduce bond strength. Chill-roll temperatures in coextrusion coating should be as hot as possible without affecting production rates. In blown-film coextrusion, the use of internal bubble cooling produces lower peel-strength values than similar structures produced without internal bubble cooling.

The thickness of the CXA is also very important. It is intuitively obvious that peel strength will suffer if the CXA layer is too thin or if it disappears altogether. On the other hand, increasing the thickness of the CXA layer beyond some critical point produces little benefit. Optimization of CXA performance requires testing to determine the minimum thickness below which a CXA's performance suffers. The best CXA will be the resin that provides a functional structure at the lowest cost. In some cases, using a thin layer of a more expensive CXA resin will be the best option.

Evaluating performance of CXA resins

In most cases, the CXA is evaluated by measuring the peel strength between layers in a multilayer structure. This is a convenient test and is suitable for quality control. However, it is vital that the converter ensure that the peel-strength analysis is representative of actual performance in end use.

One common error is to evaluate CXA functionality at room temperature, regardless of the end-use application. This is not adequate when evaluating multilayer constructions that will be exposed to higher or lower temperatures. For example, **Table VII** shows peel-strength measurements made on pouches produced from blown film both before and after retort exposure. Peel strength was measured at 21°C in both cases. CXA B-11 is clearly superior to either B-10 or A-2 considering peel strength prior to retort only. After retort, the peel strengths of B-11 and A-2 are reasonably comparable. If the pouch is to be subjected to abuse only after retort, it could be a mistake to assume that B-11 was the only functional choice.

Table VIII provides further evidence of the effect of temperature on adhesive performance. The table shows the results of a peel-strength evaluation where the side wall of a multilayer thermoformed container was subjected to dry heat. Peel strengths were evaluated on untreated samples, at elevated temperatures, and after exposure to elevated temperatures. The results indicate that A-3 and B-12 are reasonably comparable prior to the heat treatment, with B-12 producing slightly higher values. At elevated temperatures, either at 121°C or at 134°C, both CXA resins provide essentially the same resistance to delamination. However, after the cups are cooled down, B-12 provides significantly higher peel strengths.

As shown in **Table IX**, CXA performance is affected by exposure to cold temperatures as well. In this test, a polycarbonate-polyolefin film was evaluated at both 21°C and at -25°C (-13°F). Evaluation at room temperature indicates that B-9 might be the optimum choice for this application. However, low-temperature evaluation indicates that A-1 far outperforms either B-9 or L-2 in a cold environment. The converter is faced with the task of determining how much abuse the final package will encounter at low temperature compared with that at normal temperature. Once this has been determined, the choice of the optimum CXA is straightforward.

IX. Effect of temperature on peel strength of CXA resins used in blown film[a]

	Peel strength, g/in.[b]			
	21°C		*-25°C*	
CXA resin	*MD*	*TD*	*MD*	*TD*
A-1	812	875	1128	1037
B-9	1087	933	440	440
L-2	542	792	110	107

[a]Polycarbonate - CXA - Polyolefin
[b]MD = machine direction; TD = transverse direction

Extensive testing is the only way the converter can draw valid correlations between standard peel-strength measurements and performance in end use. While testing should be done in all cases, it is essential when the final package will be exposed to extreme environmental conditions.

Summary

Optimizing the performance of coextrudable adhesives (CXA) is generally a complex process. The key focus areas in this process are: selecting an appropriate resin, determining its processing requirements, and evaluating its performance in end use. Performance of the CXA resin must be considered within the combined system of package structure, conversion process, and application. The best way to maximize the performance of CXA resins is to work closely with the supplier's technical organization.☐

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