

Factors influencing adhesion in coextruded structures

Barry A. Morris

All the factors affecting adhesion must be considered when designing and producing coextruded structures.

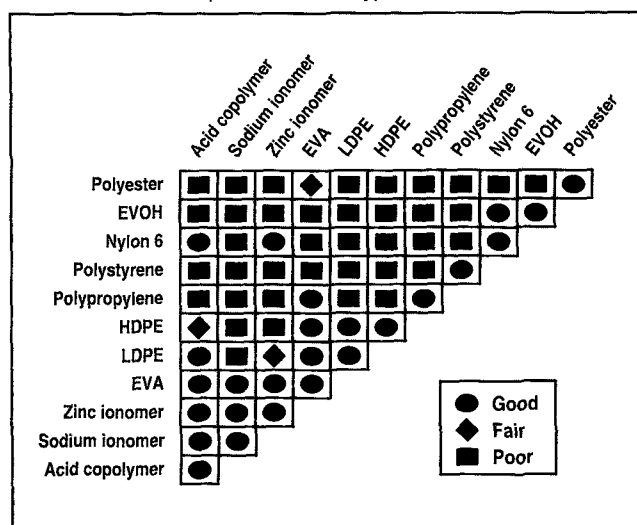
Coextrusion allows the properties of several different substrates to be combined into a cost-effective structure which often is not achievable with a single substrate. For the structure to function as a whole, there must be sufficient adhesion between the different substrates.

There are two general mechanisms for bonding at the interface of polymeric substrates: diffusion and chemical interaction. Before either mechanism can occur, the substrates must come into intimate contact. This is controlled by the surface energies of the substrates, their wettability. Optimum wettability for adhesion occurs when the polarities of the molecules of the substrates match and their surface tensions are nearly equal. Once good contact is achieved, molecular segments can diffuse across the interface to provide a strong mechanical bond, provided favorable conditions exist: the molecules are compatible (similar chemistries), the resins are above their glass transition temperatures to allow chain segment mobility, and there is sufficient time and temperature for diffusion to occur.

If conditions are not favorable for diffusion, good bonding can still occur as the result of chemical interaction at the interface. Primary ionic or covalent bonding provides strong bonding, but secondary interactions such as Van der Waals forces and hydrogen bonding are important, too. An example of a covalent bond is the formation of an ester when anhydride groups on specialized tie resins bond to the OH groups on ethylene vinyl alcohol (EVOH).

The mechanisms of debonding must be considered as well, since ultimately adhesion is defined by how easily the substrates debond. Debonding from a theoretical standpoint can be described in terms of the creation and propagation of cracks at the interface. The energy required to propagate these cracks is not only a function of the interfacial bonding due to diffusion and chemical reaction, but also is a function of the viscoelastic properties of the materials. The most common method for measuring adhesion in coextruded structures is the peel test. The force required to peel apart the layers is a function of the elongational properties of the adhesive and substrates (in addition to the interfacial bonding). In practice, this means that increasing the elongation or toughness of the

1. Relative adhesion performance of typical substrates



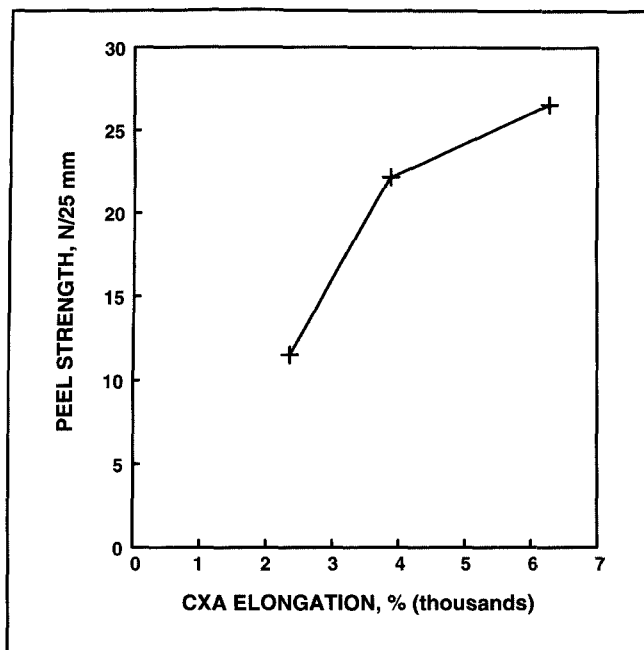
adhesive or substrate often improves peel strength.

The compatibility of the substrates and their ability to chemically interact help determine their effectiveness in bonding. **Figure 1** shows the relative adhesion performance of typical substrates used in coextruded structures. In many cases, adhesion is poor, necessitating the use of specialized adhesives called tie resins or coextrudable adhesives (CXAs). For example, a common structure in food packaging involves combining nonpolar polyolefin layers with polar barrier layers such as nylon or EVOH. Polyolefin based CXAs with anhydride or acid groups are used between these layers to promote adhesion.

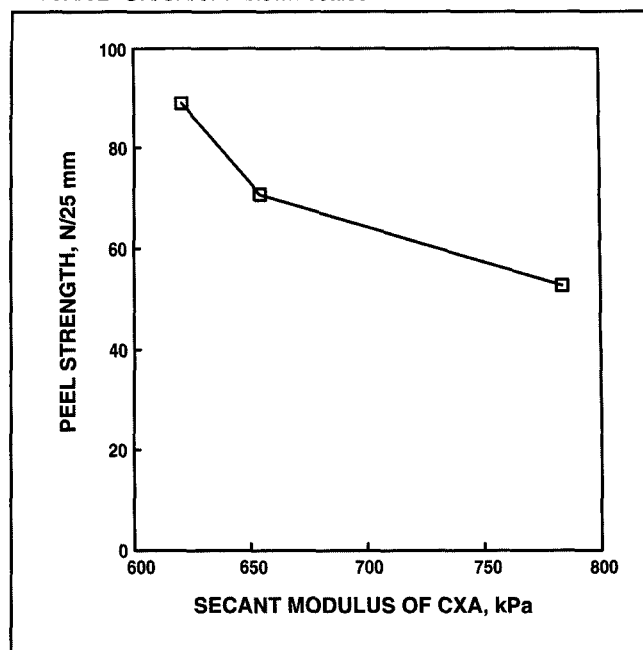
Selection of the CXA helps define the level of adhesion in the coextruded structure, but other factors also are important. The total structure design (chemical and physical properties of the individual substrates, their thickness and relative orientation), the manner in which the structure is put together (coextrusion process and heat history), and the way in which the structure is used (environmental factors and stress imparted) all play an important role. All of these factors must be considered to optimize adhesion performance.

Morris is a technical specialist at E.I. DuPont de Nemours Co., Inc., P.O. Box 80712, Wilmington, DE 19880-0712.

2. Peel performance to EVOH in PET/CXA/EVOH cast film



3. Effect of CXA physical properties on peel strength performance for PP/CXA/EVOH/CXA/PP blown bottles



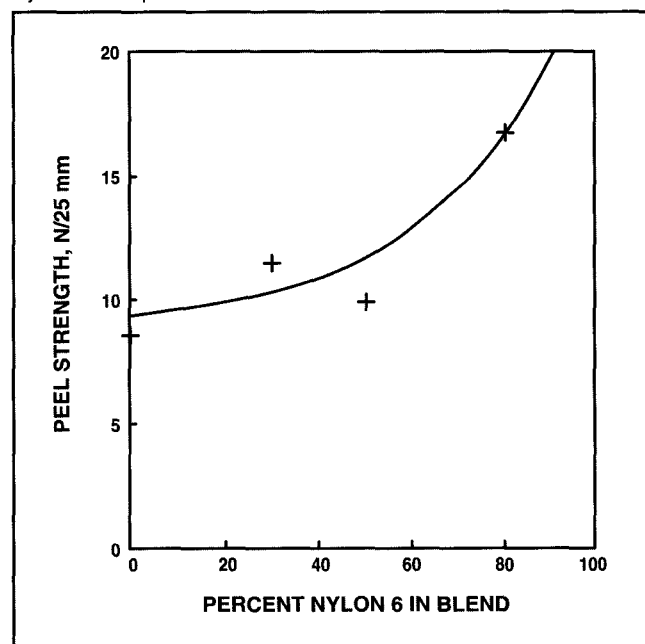
CXA selection and optimization

CXAs are specifically formulated to take advantage of the mechanisms of bonding and debonding. CXAs typically are comprised of a polyolefin matrix resin, some type of chemical functionality, and sometimes a second phase or toughener. The matrix resin provides good bonding via diffusion with polyolefin substrates. Being the bulk of the composition, the physical properties of CXAs generally reflect the properties of the matrix resin. For example, EVA-based CXAs have good clarity and formability, linear-low-density-polyethylene-based CXAs have good toughness, and high-density polyethylene and polypropylene-based CXAs have good moisture barrier properties. These types of properties contribute to the selection process since the CXA often is required to impart specific properties to the structure in addition to providing adhesion.

Chemical functionality allows bonding with polar substrates with which the polyolefin matrix resin would otherwise be incompatible. Mostly, two types of chemical functionality are utilized in CXAs: acid and anhydride. The type and level of functionality play an important role in optimizing adhesion for a given application. Acid groups bond well to aluminum foil and nylon, whereas anhydride groups bond well to nylon and EVOH. Generally, increased levels of chemical functionality improve peel strength to polar substrates, but at increased cost.

Toughening the CXA via copolymerization or alloying modifies the physical properties of the CXA and often improves peel strength. Examples of this are shown in **Figs. 2 and 3**. In Fig. 2, three experimental anhydride-modified ethylene copolymers were made with increasing levels of tensile elongation; everything else remained constant. The peel strength-to-EVOH in a three-layer cast film correlates well with the elongational properties of the adhesives. In Fig. 3, several anhydride modified polypropylenes (PPs) were prepared with different levels of toughness, as measured by their secant modulus. When

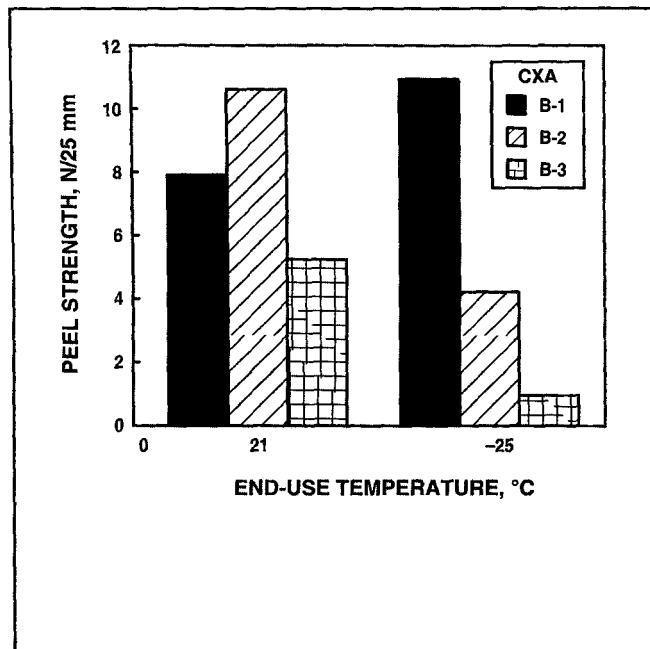
4. Effect of substrate chemistry on peel strength performance in a Nylon 6-Amorphous PA blend-CXA-LDPE film



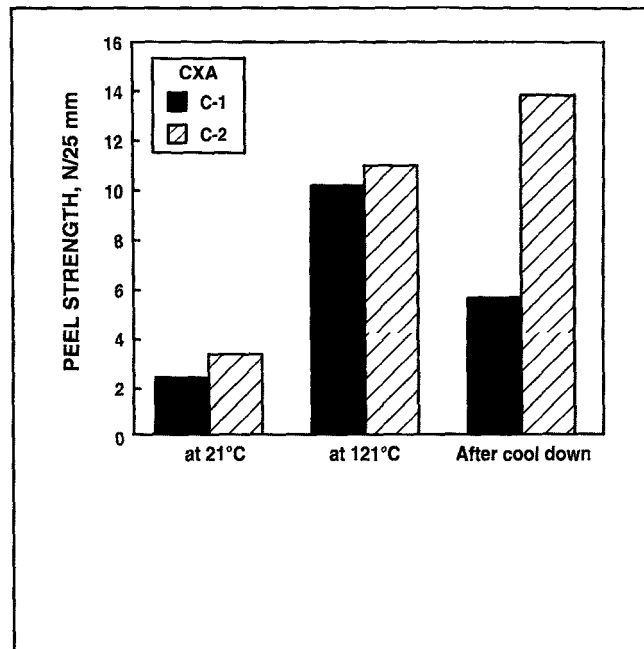
coextruded with PP and EVOH into five-layer coextrusion blow molded bottles, peel strength to the EVOH correlates well with the secant modulus of the adhesive.

The selection of a CXA depends on a number of things, including its peel strength performance to the substrates in the structure, its processibility, how it affects the performance of the structure (WVTR, toughness, clarity, etc.), and its cost. Working with the technical group of a CXA supplier can help users make the proper selection.

5. Effect of end-use temperature on peel strength in PC-CXA-Polyolefin blown film



6. Effect of temperature on peel strength



Structure design

The selection of a CXA should not be made only by considering the substrates to which the CXA will bond. CXA performance is highly dependant on the structure in which it is incorporated, how that structure is made, and how it is ultimately used. Some of the factors that must be considered while designing the structure are the chemical and physical properties of each of the substrates and the thickness of the layers.

Figure 4 shows how the chemical properties of a substrate can affect adhesion. Here, peel strength to a blend of amorphous nylon and nylon 6 in a three-layer, coextruded blown film is given as a function of the amount of nylon 6 in the blend. As the level of nylon 6 is increased, peel strength increases. This shows that all nylons do not bond alike. This is true of other substrates as well, particularly solid substrates used in extrusion coating or lamination. Here, surface properties are extremely important and can vary widely depending on manufacturing conditions.

Increasing the thickness of the adhesives or substrates often improves peel strength because of increased energy to bend the sample, among other things.

Processing considerations

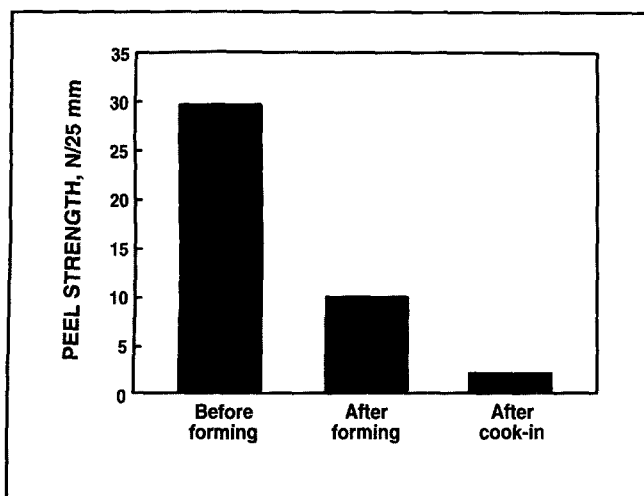
The conversion process has an impact on adhesion by the amount of residual stress imparted and the time and temperature at which molten layers are in contact. It is difficult to generalize which processes may be more stringent on adhesion. Typically, less orientation and longer contact times at higher temperatures favor greater adhesion.

Several processing parameters are important for optimizing adhesion, including extrusion temperature, contact time, cooling rate, and forming temperature:

- Generally, hotter is better for adhesion. Diffusion and chemical reaction at the interface increase with increasing temperature and contact time. Of course, temperatures must be moderated in consideration of the thermal stability of the adhesive, thermal stability of other substrates, and viscosity matching.
- Increasing melt contact time generally improves adhesion. Combination technology (feedblocks in many cases offer longer contact time than multimanifold dies), the order in which layers are brought together, and land length after the streams have been combined play an important role.
- Increasing line speeds reduces contact time and generally results in lower adhesion.
- Heat transfer and rate of quench are important in terms of reduction of time at elevated temperatures and its effect on crystallization. Decreasing the chill-roll temperature in flat-film or sheet coextrusion, or using inner bubble cooling in blown film, tend to reduce interlayer contact time at elevated temperatures and reduce adhesion.
- Orientation generally lowers adhesion. Increasing the blow-up ratio in blown-film or increasing line speed in flat-film extrusion usually results in lower adhesion. Peel strength measured in the direction of orientation often is less than in the transverse direction.
- Forming temperature may also be optimized for improved performance. As forming temperature is increased, peel strength increases. As forming temperature is increased, less residual stress is believed to be imparted.

Many of these factors run contrary to increased production rates. For maximum productivity, getting heat out of the

7. Effect of cook-in on peel strength in Nylon-CXA-ionomer film



system is paramount. This may mean not putting as much heat in to begin with and faster quench rates, which have a negative impact on adhesion. It is important to recognize and understand this relationship between adhesion and production rate.

Because of differences in heat transfer, cooling rates, contact times, etc., between lab lines and production lines, as well as between one production line and another, adhesion always should be tested on product made on the actual production line when developing a new structure.

End-use considerations

The manner in which a structure will ultimately be used can have a significant impact on performance. Care must be taken to test the structure under conditions closely simulating its end use. Factors such as end-use temperature and environment affect peel strength performance.

Figure 5 shows the results of the evaluation of three CXAs in a PC-CXA-polyolefin blown film at room temperature. B-2 gives the best peel strength, but when measured under the expected end-use storage conditions of -25°C , B-1 is the best adhesive.

Figure 6 shows another example of the effect of temperature on peel strength. Here strips from the side wall of a solid-phase, pressure-formed container with the structure

PP-CXA-EVOH-CXA-PP were placed into a tensile tester equipped with an environmental chamber. The peel strength was measured at room temperature. The chamber was then heated to 121°C for one hour (conditions typical of retort sterilization) and the peel strength measured again. After the sample was cooled back down to room temperature, the peel strength was measured once again. In this particular example, the peel strength increased at the higher temperature, perhaps due to annealing out of the residual stresses. After cool down, C-2 gave substantially better adhesion than C-1.

Another extreme end-use environment is cook-in applications where ham or poultry is cooked inside a multilayer film at $70\text{--}80^{\circ}\text{C}$ for up to several hours, as shown in Fig. 7. Here a three-layer blown film (PA-CXA-ionomer) is evaluated. The first step is to form the film into a cavity into which the meat is placed. Forming alone reduces adhesion due to orientation and thinning effects. During cooking, adhesion can be reduced further due to the extreme stresses and temperature associated with this process.

Conclusion

Adhesion in multilayer structures is a complicated process affected by many factors. Careful consideration of the substrates that make up the structure, the process in which the structure is made, and testing the product in its end use can result in optimal performance. The converter has control over the design of the structure and processing parameters. CXA suppliers bring knowledge of how their materials bond to different substrates under different processing and end-use conditions. By understanding what the end user needs in terms of end-use performance and how the end-use environment affects adhesion, the converter can begin to optimize the structure and process to meet those needs. □

Conversion Factors:

$\text{N/25 mm} \times 0.22 = \text{lb/in.}$

$\text{kPa} \times 0.15 = \text{kpsi}$

$\text{N/25 mm} \times 102 = \text{g/in.}$

Received for review Jan. 20, 1992.

Accepted Feb. 14, 1992.

Presented at the TAPPI 1992 Coextrusion Short Course.

Keywords: Adhesion, coextrusion, chemical properties, physical properties, substrates, structures, multilayers, end use, processes.